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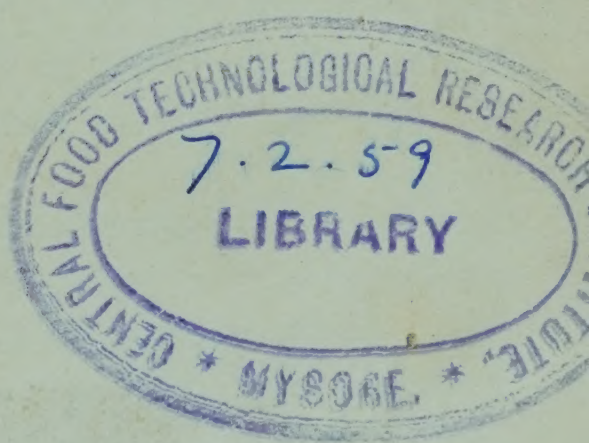
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CUMMING AND KAY
'QUANTITATIVE
CHEMICAL ANALYSIS'

ELEVENTH EDITION REVISED BY
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FOREWORD

BY

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DR KAY, whose colleague I was for several years before his untimely death in 1933, was a firm believer in a thorough grounding in the so-called classical methods of inorganic analysis, that is, in methods concerned primarily with the chemical properties of substances. To-day, however, besides all the new chemical methods of analysis, a bewildering array of physicochemical and instrumental methods confronts the analytical chemist, complicating the issue regarding what should now be taught.

It is, I think, generally conceded by analytical chemists, even those most highly versed in the use of instrumental techniques, that specialised instrumentation should not be introduced in teaching courses until physical and physicochemical principles have been mastered, and that a basic training in classical methods provides the best foundation on which to build, more especially as so many of the current instrumental techniques depend upon chemical methods for the establishment of standards.

Dr Chalmers, who has had considerable industrial and academic experience and is a competent and enthusiastic analytical chemist and teacher, has wisely decided that instruction in the more fundamental aspects of analytical chemistry must still be the primary aim in teaching and the main feature of this book. Several new methods have, however, been inserted, and numerous conventional procedures have been modernised. References to the original papers are given for some important methods that have not been described in detail.

Physicochemical and instrumental methods have not, of course, been neglected. The thoroughly revised section on photometric methods demonstrates clearly the value of instruments in this very important branch of analysis. A new section on physicochemical methods, although brief, is sufficient to whet the appetite of the reader, who will no doubt desire to study the various subjects further.

Since it is highly desirable that the student should become familiar with the literature of analytical chemistry, the lists of suggested reading matter at the end of several sections are a welcome addition to the book.

EXTRACT FROM PREFACE TO FIRST EDITION

THIS book is intended primarily for University and College students. We have endeavoured to arrange the book in such a manner that some knowledge of the principles of Quantitative Analysis may be acquired by a practical study of the subjects included in Parts I., II., and III., and that the further requirements of those who are making a special study of Chemistry should be met by the later portions of the book.

Most of the typical exercises in Parts II. and III. may be performed with pure substances, but it is desirable that the student should be accustomed from the commencement of his course to the analysis of substances of "unknown" composition. The serious student finds that this enhances the value of the exercise, whilst the occasional student who "only wants to know the method" has his attention directed to the real purpose of Quantitative Analysis. A list of solutions suitable for analysis is given in the Appendix. In describing typical exercises, care has been taken to give the practical details of manipulation as fully as possible, and where full details are not given, reference is invariably made to the pages where they may be found.

In Part V., all the common elements and radicals are considered, together with the methods for their separation and determination. As the arrangement is alphabetical and copious references to other parts of the book are given, it is hoped that this section will prove a useful index.

In order to avoid constant repetition of particulars in regard to the concentration of reagents, it has been assumed throughout the book that, unless the contrary is stated, the concentration of a reagent is that specified in the Appendix. The concentrations usually recommended for indicator solutions are such that even

"a few drops" is often more than ought to be used. The concentrations recommended in the Appendix are so chosen that 1 c.c. of the indicator is the normal amount required, and throughout the book it is assumed that these dilute indicator solutions are used.

All the diagrams have been specially drawn for the book—in a large number of cases from original photographs of the apparatus.

CHEMISTRY DEPARTMENT

UNIVERSITY OF EDINBURGH

October 1913

PREFACE TO THE ELEVENTH EDITION

AS a result of various circumstances the task of revising this book has passed into new hands. The present reviser hopes that he has maintained the traditions of the text.

Among the major alterations in this edition may be listed the rewriting of the section on colorimetry, the writing of a brief account of the theory of precipitation and contamination of precipitates, the deletion of the section on water analysis (on the ground that this is a specialist topic best served by the appropriate texts), and its replacement by a short and elementary account of some of the physicochemical methods that are now used more and more often. The remainder of the text has been revised and brought up to date where this was thought necessary. Many methods are included by giving references to the literature but it was not thought practicable to find and give references for the older methods. An innovation is the inclusion of short lists of suggested reading matter.

The account of the measurement of volumes of liquid and the standardisation of volumetric instruments has been brought into line with the appropriate British Standard Specifications. Data from these Specifications are quoted in the text by kind permission of the British Standards Institution.

The reviser's thanks are due to Dr Christina C. Miller for her helpful advice, Mr D. D. K. Grant for the method on p. 505, Dr E. S. Page for advice on statistical calculations, Mr P. M. Booth for advice on conductometric titrations, Dr S. J. Thomson and Dr N. Sutin for reading the revised text and making helpful suggestions, and Miss M. Z. O. Seddon for assistance in reading the proofs. The responsibility for errors and omissions, however, rests entirely with the reviser.

DEPARTMENT OF GEOLOGY
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1955

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QUANTITATIVE CHEMICAL ANALYSIS

PART I

GENERAL PRINCIPLES

IT is perhaps no exaggeration to say that the whole structure of the science of chemistry has been built on the foundations laid by analytical chemists. The practice of analytical chemistry has played a fundamental role in the elucidation of the composition and structure of chemical compounds, and in the formulation of the laws of physical chemistry. The analytical chemist must have a sound knowledge of chemistry as a whole, and must be willing and able to press into service useful techniques derived from other branches of the science. Specialists in the other branches of chemistry must also have a proper knowledge and appreciation of analysis so that they may ask the right questions of it and interpret correctly its results.

Qualitative analysis is the identification of the constituents of a substance, and quantitative analysis is the determination of the relative amounts of them present. The methods of quantitative analysis fall into well-defined groups; the type of method chosen for a particular determination depends on the conditions peculiar to that determination.

The gravimetric method of analysis usually involves (1) the separation of the constituents of the substance in the form of insoluble compounds of known composition; (2) the determination of the weight of the compounds so obtained.

The volumetric method of analysis, on the other hand, is based on the use of a reagent of known concentration, and on the measurement of the volume of this reagent required to complete the chemical change involved.

The colorimetric method of analysis depends on the measurement of the intensity of colour of a solution of a coloured compound derived from the element being determined, and on the relationship between the intensity of colour and the concentration of the solution.

A fundamental distinction between the three methods is that *in gravimetric analysis* the constituent that is to be determined must be separated from all the other constituents of the substance, whereas *in volumetric or colorimetric analysis* the separation of the constituents is frequently unnecessary, and one or more of the constituents of a substance can often be rapidly determined in the presence of all the others, thus greatly simplifying the analytical procedure.

Most substances can be determined by all three methods, the choice being governed by various factors. Colorimetric analysis is most useful for the determination of small amounts of substances, or for rapid analysis for control purposes. Unless special techniques are used the method is not well suited to the determination of substances present in major amounts. Volumetric methods are generally used when rapid and accurate analysis is required. Gravimetric methods are usually employed when it is necessary to use the same sample of material for several determinations, the analysis being conducted by a series of quantitative separations by precipitation.

Besides the classical methods of analysis just mentioned, the chemist may use physical methods of analysis such as polarography, spectrography, electrochemistry, and radio-activation. He may also make separations by such techniques as solvent extraction, distillation, and chromatography.

In the systematic treatment of the subject it is convenient to consider types of analysis separately, but in practice the different methods of procedure are often combined in order that the analysis may be completed as rapidly and accurately as possible. In choosing the method to be used for the determination of a substance it is necessary to consider the nature of the sample. Most materials met with in practice are complex, and the chemical behaviour of some components may vitiate the determination of others if their presence is ignored. Consider the determination of titanium colorimetrically by means of the method involving hydrogen peroxide. If vanadium is also present, the coloured pervanadate ion will interfere in the

determination, and high results will be obtained unless the analytical procedure is modified to eliminate the effect of the vanadium.

A prime aim of analytical research is to develop methods that are specific for individual elements or groups, and hence are applicable to a wide range of materials without modification.

THE BALANCE

For accurate analytical work, a balance, capable of supporting a maximum load of 100 to 200 grams in each pan, is indispensable. It is important that the maximum load, whatever it may be, should never be exceeded. With a good balance, properly adjusted and used, very accurate measurements can be made. For example, it is possible to distinguish between two masses of about 10 grams each when they differ in weight by only 0.1 milligram, *i.e.* by 1 part in 100,000. A balance is, therefore, a delicate instrument of precision, and the greatest possible care must be taken in using it. *The rules regarding the use of the balance (p. 12) must be carefully read and thereafter strictly adhered to.*

When weighing in a comparatively rough fashion, it is generally assumed that equipoise is established when the excursions of the pointer towards either side of the mid-point of the scale are of equal amplitude. For the following reasons, however, this method is not invariably adopted in accurate work.

- (1) The zero-point, or resting-point of the unloaded balance, *i.e.* the position which the pointer would apparently take up if the oscillating beam were allowed to come to rest, seldom coincides exactly with the mid-point of the scale.
- (2) Since the oscillating beam, if left to itself, ultimately comes to rest, the amplitude of each oscillation, even when equipoise is established, is *less* than that of the preceding one. It follows that, if an excursion of the pointer to the left is equal to the preceding one to the right, the weight on the right is greater than that on the left (assuming that the zero-point coincides with the mid-point of the scale).

Routine Method of Weighing

In making a weighing, accurate to 0.1 milligram (0.0001 gram), the following methods may be used :—

· *The method of swings :—*

(1) Find the *zero-point* of the balance.

Release the beam carefully, and if necessary set it oscillating so that the pointer moves through about five scale divisions on either side of the mid-point. To do this, open the balance-case gently, waft air down onto one of the pans, and close the case again. With practice, careful manipulation of the release mechanism will produce the desired swing. Neglect the first two complete oscillations (four excursions of the pointer; this allows air currents to die down) and then carefully observe and note down the next *five* extreme positions of the pointer, that is, three turning points on one side and two on the other. Assume the scale to be numbered from the extreme left towards the right, *e.g.* from 0 to 20, the mid-point being 10, and estimate tenths of scale divisions.

If, for example, the observations were

Left.	Right.
(1) 5.0	
	(2) 15.8
(3) 5.4	
	(4) 15.4
(5) 5.8	

the resting-point will be midway between the mean turning-points on left and right, and is therefore

$$\frac{5.4 + 15.6}{2} = 10.5$$

One more reading must be made on one side than on the other to allow for damping of the swings by air resistance and friction in the working parts. The resting-point is taken as the zero-point of the balance. If the observations are repeated several times the results should not differ by more than one or two tenths of a scale division. As the zero-point is frequently subject to slight fluctuations, it should be determined before each set of weighings is begun, and checked when the set is completed.

(2) Place the vessel to be weighed on the *left* pan of the balance and proceed to counterpoise it. It is best to begin with a weight that will probably be too heavy, as this may save time in the end. For example, if the weight of the vessel is thought to lie between 15 and 20 grams, the latter weight is placed on the right scale-pan. If, on releasing the beam, the 20-gram weight is seen to be too much, it is replaced by a 10-gram weight. If this is insufficient the 5-gram weight is added, and the deflection tested. This and smaller weights are added or removed systematically in decreasing order of size until the sum of the weights on the right-hand pan is such that another 0.1 gram would bring about a deflection of the pointer to the left of the zero-point.

The residual difference in weight is measured by means of a rider—a piece of wire shaped to fit on the beam, and weighing either 5 or 10 milligrams. The effective weight of the rider depends on its position on the beam. A 5-milligram rider is used on a balance which has a beam divided into ten equal divisions from left to right of the beam; a 10-milligram rider is used on a balance having a beam divided into twenty equal divisions, ten on either side of the mid-point of the beam. A 5-milligram rider must always be placed on the beam at division 0 when the zero-point is determined; transfer of the rider to division 10 is equivalent to a change in weight of 10 milligrams.

After adjusting the weights, close the balance-case, and place the rider in such a position that equipoise is nearly established—for example, at division 3. After some experience it will be found possible to estimate approximately, by observing the rapidity of the movement, what additional weight is required to establish equilibrium. If, for instance, it has been found that with 16.46 grams on the pan the pointer is deflected slowly to the right whilst with 16.47 grams it is deflected much more rapidly to the left, the weight of the object is nearer 16.46 than 16.47 grams. If it is necessary to change the position of the rider, the beam should be arrested before making the change. Determine the resting-point as before by recording five turning-points of the pointer. Suppose it is found to be 9.6 with the rider at division 3.

(3) Find the “sensitiveness” of the balance, *i.e.* the displacement of the resting-point produced by an alteration of 1 milligram:—Alter the position of the rider by an amount

corresponding to 1 milligram—in such a direction that the resting-point is shifted to the other side of the zero-point—and again determine the resting-point. Suppose it to be 11.1 when the rider is at division 2. The sensitiveness is then equal to

$$11.1 - 9.6 = 1.5 \text{ scale divisions per milligram.}$$

(4) Now calculate, as follows, the alteration of the weight necessary to counterpoise the vessel exactly :—

The zero-point—using the figures assumed in the foregoing—is 10.5, and the resting-point with a load of 16.462 grams is 11.1. The vessel weighs, therefore, more than 16.462 grams, the additional amount being equal to that necessary to displace the resting-point from 11.1 to 10.5, or 0.6 of a scale division. Since, however, 1.5 scale divisions correspond to 1 milligram, 0.6 scale division is equivalent to

$$\frac{0.6}{1.5} = 0.4 \text{ milligram.}$$

The weight of the vessel is therefore 16.4624 grams.

The complete weighing thus involves the determination of three resting-points—the first, that observed with the empty balance ; the second, after approximately counterpoising ; the third, after making an alteration of ± 1 milligram. All the observations made in the above example are shown below :—

<i>Resting-points</i>			
	(1) Unloaded balance.	(2) With load of 16.463 grams.	(3) With load of 16.462 grams.
	5.0	4.4	6.7
	15.8	14.7	15.3
	5.4	4.6	7.0
	15.4	14.5	15.1
	5.8	4.9	7.3
Mean	5.4 15.6	4.6 14.6	7.0 15.2
Resting-points	10.5	9.6	11.1
Sensitiveness	= 11.1 - 9.6 = 1.5 scale divisions		
Deviation	= 11.1 - 10.5 = 0.6 „ „		
Additional weight	$= \frac{0.6}{1.5} \times 1 \text{ milligram} = 0.4 \text{ milligram}$		
Weight of vessel	= 16.462 grams + 0.4 milligram		
	= 16.4624 grams		

The method of short swings :—

If the amplitude of swing of the pointer is of the order of two to four divisions on either side of the mid-point of the scale,

the decrease in amplitude at each swing is usually so small that the mean of two successive turning-points will coincide with the zero-point determined by the method of swings, within the limits of observational error. In the case of the zero-point considered above, the zero-points determined by short swings would be 10.4 or 10.6 according to which pairs of turning-points were chosen. These values are within a tenth of a scale division of the zero-point previously determined. This small error can be eliminated by observing the turning-points always in the same order ; the error will then occur in the same direction in the zero-point and in the resting-point for the weighing of the object, and will cancel in the calculation of the deviation.

Determination of the Sensitiveness of the Balance with Different Loads

It is evident from the foregoing that the process of weighing may be considerably shortened if the sensitiveness of the balance is already known. The sensitiveness usually varies with the load, and may either increase or decrease with the load, according to the construction of the balance. Good modern balances are so constructed that the sensitiveness is practically constant for all loads up to the limit for which they are intended to be used.

Determine, then, the sensitiveness with 5, 10, 20, and 50 grams in each pan. There is some advantage in placing an excess of 5 mg. on the left scale-pan in order that equipoise may be established with the rider near the middle of the right arm of the balance. The resting-point is then determined with the rider in two positions, differing by 1 or by 2 milligrams, and so chosen that the resting-points are found on opposite sides of the zero-point. From the observations calculate the sensitiveness with each load, that is, the displacement of the resting-point produced by an alteration of ± 1 milligram, and keep a record of the results in a note-book.

When the sensitiveness has been determined in this way, once for all, the process of weighing consists of the following two operations :—

- (1) Finding the zero-point of the balance.
- (2) Counterpoising the object to the nearest milligram and finding the resting-point.

The fraction of a milligram that must be added (or subtracted) to complete the counterpoise is then calculated. If, for example, the zero-point is 10.2, the resting-point 9.7 with a weight of 5.826 grams, and the sensitiveness 1.7, then the correct weight is $\frac{10.2-9.7}{1.7} = \frac{0.5}{1.7} = 0.3$ milligram less than the weight on the balance-pan ; that is, 5.8257 grams.

Abbreviated Method of Weighing

It is often permissible, in practice, to shorten the routine method of weighing and thus to save time, without sacrificing the necessary accuracy. The abbreviated procedure varies with the circumstances, as follows :—

- (1) When the required weight is to be ascertained by “difference,” *e.g.* the difference between (a) the weight of an empty vessel, and (b) the weight of the vessel and substance, *and when the two weighings involved are consecutive*, the zero-point of the balance may be assumed to be 10 for both weighings. The same error (if any) will appear in both weighings, but the difference will give the accurate weight of the substance.
- (2) It is not always necessary to weigh a sample to the fourth decimal place. It is sufficient to weigh it with a precision that is about five times as precise as that of the final operation in the analysis. If the final product weighs, say, 100 milligrams, it can be weighed with a precision of about 2 parts per 1000. It is then sufficient to weigh 1 gram of sample to the nearest milligram ; the weight of the sample will be in error by not more than 0.5 milligram, a precision of 0.5 parts per 1000 (*cf.* p. 25).

Sources of Error in Weighing

The following factors must be taken into consideration in accurate weighing :—

- (1) The effect of inequality in the length of the right- and left-hand arms of the balance.

- (2) The effect of buoyancy of the air on the object and weights.
- (3) A possible change in the weight of the containing vessel between successive weighings.
- (4) A possible change in the weight of the substance being weighed.
- (5) Errors in the value of the weights themselves.

These errors may be eliminated as follows :—

(1) The error caused by unequal lengths of balance-arms is proportional to the load, and in weighing small objects it can usually be neglected, when a good balance is used. Also, the error will be nearly eliminated when weighing a vessel empty and then with a gram or so of material, provided the vessel is always placed on the same pan of the balance. The error can be completely eliminated by the tare method, or by the method of double weighing. In the former, the object is counterpoised by a spare set of weights which need not be accurate ; accurate weights are then substituted for the object. In the latter method, the object is first put on the left-hand pan, and the apparent weight W_1 is obtained with accurate weights on the right-hand pan. The object and weights are then interchanged, and the apparent weight W_2 found with the accurate weights on the left-hand pan. If x equals the true weight of the object, and R and L are the lengths of the right-hand and left-hand arms respectively, then

$$xL = W_1R, \text{ and } xR = W_2L.$$

By multiplying these equations together, and eliminating RL from both sides, we obtain

$$x^2 = W_1W_2, \text{ or } x = \sqrt{W_1W_2}$$

Since in practice W_1 and W_2 are very nearly equal, x may be taken as $\frac{W_1 + W_2}{2}$.

If a particular balance shows a serious error from inequality in the length of the arms, it is convenient to draw a graph showing the relation between the apparent weight obtained by a single weighing, and the weight obtained by the tare or the double-weighing method.

(2) The buoyancy of air introduces a considerable error if the density of the object being weighed differs greatly from

that of the weights, though, unless great accuracy is necessary, the error arising from this cause may be neglected in the case of a solid whose weight is not more than 0.5 gram. No further error is, of course, introduced by the volume of the container which is weighed with and without the solid. It is, however, essential to correct for the air displaced when weighing considerable volumes of a material of low density, and especially in weighing vessels containing gases. The true weight, *i.e.* the weight *in vacuo*, is given by the following formula to a very close approximation :—

$$W_x = W_a + W_a \times D_a \left(\frac{1}{D_s} - \frac{1}{D_w} \right)$$

where W_x is the true weight, W_a the weight in air, D_s the density of the substance being weighed, D_w the density of the weights used, and D_a the density of air (*i.e.* the weight of 1 millilitre (see p. 524) under the conditions of temperature, pressure, and humidity obtaining, usually about 0.0012 gram).

(3) The weight of the containing vessel may have changed by adsorption or loss of moisture, and it may also show an apparent change in weight because of electrification of the surface or because its temperature differs from that of the balance-case.

Errors arising from changes in the amount of moisture adsorbed on the surface may be largely eliminated by wiping the vessel gently with a linen cloth, and allowing it to stand twenty minutes or more in the balance-room before weighing. A better method is to use a *tare* as a counterpoise. The tare is a vessel as much like the vessel to be weighed as possible. It is given exactly the same treatment as the vessel to be weighed and so is exposed to the same influences. Any errors arising from adsorption of moisture or changes in humidity cancel one another.

Errors caused by electrification of the surface are more likely to occur in borosilicate than in soft glass vessels, and even more so in vessels made of quartz or fused silica. The electrification may be caused by rubbing or merely by heating. The electrification may be discharged in a number of ways, such as exposure to ultra-violet light or a high-frequency discharge or ionising radiation. A recommended method is to keep in the balance-case a two-inch strip of Tl^{204} or $Sr^{90} + Y^{90}$ foil. These radio-isotopes emit β -particles which discharge the

surface electrification by ionisation of the air in the balance-case.

Errors arising from temperature differences are avoided simply by allowing adequate time for the establishment of temperature equilibrium. The existence of a temperature difference will usually be made manifest by a drift in the turning-points. The turning-points on one side may show a regular decrease in the amplitude of swing while those on the other side show an increase or remain stationary. The presence of electrification is often shown by a general irregularity in the turning-points or a drift similar to that just mentioned. It is to detect such errors that it is recommended that *five* turning-points should be observed.

If the container is weighed at first when filled with air, it is advisable to make subsequent weighings when it is again filled with air, unless a correction can be calculated to allow for the presence of a gas of different density.

(4) Hygroscopic, efflorescent, and volatile substances should, of course, be weighed in closed vessels, and it should be remembered that finely divided dry powders will rapidly pick up moisture in the air. In such cases a drift of turning-point will be observed.

(5) It is usual to determine the errors in the weights themselves as described on p. 13, but if these are excessive, the errors can be reduced by the following procedure.

At least one standard weight must be available, and the absolute values of the individual weights must first be determined by means of this. Good weights of one gram and upwards have screwed-in knobs for lifting, and by unscrewing these with leather-covered pliers, adjustments may be made by adding or removing packing material. The most suitable material for this is wire made of nickel-chromium alloy, as this is resistant to corrosion and has approximately the same density as brass.

Platinum fractional weights can be reduced in weight by carefully rubbing an edge on fine carborundum. Their weight can be increased by connecting them to the positive pole of a 12-volt accumulator, and touching them momentarily with the edge of a piece of platinum foil connected to the other pole through a resistance of about one ohm. Contact between the weight and the copper lead should be made through tightly held platinum foil.

Rules to be Observed in Using the Balance

It should be remembered that one incorrect weighing spoils the whole analysis.

- (1) The object to be weighed must be at room temperature. If it has been heated, sufficient time must be allowed for it to cool. The time required to attain the room temperature varies with the size, etc., of the object, but as a rule thirty minutes is sufficient.
- (2) Glass vessels, after being handled, should be wiped with a linen cloth, and then left in the balance-room for at least twenty minutes before weighing. This is necessary more especially in the case of large vessels, such as flasks, U-tubes, etc., the weight of which may vary by several milligrams according to the conditions under which they are weighed.
- (3) Chemicals to be weighed should never be placed directly on the balance-pan, but in a weighing-bottle or on a watch-glass or scoop. When it is necessary to add more of a solid or liquid, the operation must be performed outside the balance-case.
- (4) Liquids and volatile solids must be weighed in a closed vessel, such as a stoppered weighing-bottle. If the vapour is corrosive, the vessel should not be opened in the balance-room.
- (5) The operator should sit opposite the middle point of the balance.
- (6) The beam should be released and arrested gently, and, if necessary, set swinging by a draught of air (see p. 4). The pans must not swing from side to side.
- (7) The zero-point of the balance should be determined before each set of weighings.
- (8) The pointer should swing through four or five divisions beyond the mid-point of the scale. The pans must on no account be touched while the beam is swinging.
- (9) The weights must be lifted with the forceps only.
- (10) The balance must be arrested before anything is placed on the balance-pan or removed from it.
- (11) The balance-case must always be closed before the rider is used.

- (12) The weight should be recorded in a note-book (not on a loose slip of paper, which might be lost) before the weights are removed from the pan. The weight should be noted from the empty places in the box, and checked as the weights are returned from the pan. At the end of the weighing the rider must be placed in the zero position or removed from the beam according as it is a 5- or a 10-milligram rider.
- (13) Nothing should be left on the pans when weighing is finished. Any chemical spilt in the balance-case must be removed at once.
- (14) The balance-case should be closed when weighing is finished.

Exercises in Weighing

Read the description given of the routine method of weighing (pp. 4 to 8), study carefully the rules to be observed in the use of the balance, and then practise the following exercises in order to become familiar with the balance and the method of using it. Make notes of your observations and submit them for inspection.

- (1) Find the zero-point of the balance. Repeat the operation four times (at least), arresting the balance after each. Keep a record of your observations as shown on p. 6.
- (2) Find the sensitiveness of the balance with loads of (*a*) 5 grams, (*b*) 10 grams, (*c*) 20 grams, (*d*) 50 grams in each pan.

Tabulate the results and draw a graph showing the variation of sensitiveness with the load.

- (3) Clean a porcelain crucible and lid. Weigh to 0.1 milligram, (*a*) the crucible, (*b*) the lid, (*c*) the crucible and lid. Keep a record of all the observations from which the zero-point, the various resting-points, and the final results are obtained.

CALIBRATION OF WEIGHTS

Reference has been made to possible errors in the weights themselves. Since in most cases only *mass ratios* and not *absolute masses* are of importance in analytical chemistry, it is not essential that the unit weight adopted should exactly

represent a true or standard gram ; but it is imperative that the various pieces in a set should agree amongst themselves, *e.g.* that each of the 1-gram weights should be exactly 100 times the weight of each centigram, and one-tenth that of each 10-gram piece. Another essential for a good set of weights is constancy of mass. Brass weights require a protective coating to prevent corrosion. Neither lacquer nor gold plating is now regarded as a very satisfactory protection. Chromium plated weights give much better service but probably the best results are obtained with rhodium plating. There is a tendency to replace brass weights by those made of nickel and chromium alloys and by certain types of stainless steel, containing a little manganese and molybdenum in addition to nickel and chromium. It is important that such alloys should have approximately the same density as that of brass, *i.e.* 8.4, since buoyancy correction tables are based on the assumption that the weights used have this density. Some of these alloys which have densities of about 8.4 give excellent results. They are non-magnetic, highly resistant to corrosion, and do not adsorb moisture from the air.

It ought to be an invariable rule to test a set of weights before it is used for accurate work. The integral weights in a set usually comprise the following pieces :—

50, 20, 10', 10'', 5, 2, 1', 1'', 1'''.

The weights of the same nominal value are usually provided with distinguishing marks ; if there are none, one or more *minute* marks must be made upon them with the point of a knife before beginning the calibration. Some modern sets of weights contain pieces weighing 50, 30, 20, 10, 5, 3, 2, and 1 grams, with corresponding values in the fractional weights. The fractions in these sets are made of wire bent into shapes that indicate the value of the piece (the 0.3 and 0.03 gram weights are in the form of triangles). The advantage of these sets is the absence of confusion between weights of the same nominal value, and the ease of recognition of values of fractions. These weights are calibrated in the same way as the older sets, the comparison of the weights being made by the method of "double weighing" (see p. 9). The procedure is as follows :—

Find the zero-point of the balance. Place the 50-gram weight on the left scale-pan and the remainder of the integral

weights on the right. Determine the resting-point. If it differs from the zero-point, find, by the method already described, what additional weight must be added to either side of the balance in order to give exact counterpoise. Now interchange the weights, placing the 50-gram weight on the right, and again determine the difference between the loads. If, for example, the two weighings were

Left.

Right.

$$50 + 2.0 \text{ mg.} = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''',$$

$$\text{and } 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' = 50 + 0.4 \text{ mg.,}$$

the average of the two weighings is

$$50 + 1.2 \text{ mg.} = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''',$$

$$\text{or } 50 = 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1''' - 1.2 \text{ mg.}$$

In the same way, compare the 20-gram weight with the sum of 10' and 10'', 10' with 10'', and 10' with the sum of 5, 2, 1', 1'', and 1'''.

As the effect of inequality of the arms varies with the load, if it is found at this stage with 10 grams in each pan that the difference between two weighings is not more than 0.2 milligram, only one weighing need be made in comparing the smaller weights. Proceed then, further, to compare the 5-gram weight with the sum of 2, 1', 1'', and 1'''; the 2-gram weight with 1' + 1'', and also 1'' with 1', and 1''' with 1'.

In the first and second columns of the following table the

Nominal value of weights.	Observed results of double weighings.	Calculated value of each piece in terms of weight marked 1'.
1'	= provisional unit.	= 1' mg.
1''	= 1'	= 1' - 0.1
1'''	= 1'	= 1' + 0.1
2	= 1' + 1''	= 2 × 1' - 0.1
5	= 2 + 1' + 1'' + 1'''	= 5 × 1' - 0.3
10'	= 5 + 2 + 1' + 1'' + 1'''	= 10 × 1' - 0.9
10''	= 10'	= 10 × 1' - 1.1
20	= 10' + 10''	= 20 × 1' - 2.5
50	= 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 50 × 1' - 6.1
Total 100	= 50 + 20 + 10' + 10'' + 5 + 2 + 1' + 1'' + 1'''	= 100 × 1' - 11.0

results obtained with a set of weights are arranged in order, beginning with the small weights.

If no standard weight is available, select, as a provisional

unit, one of the single gram pieces, say $1'$, and express the value of each of the others in terms of this unit. The result of this is shown in column 3. The transformation is easily made if the successive rows are extended in order, beginning with the first. For instance, the 5-gram weight is equal (see column 2) to the sum of the preceding weights minus 0.2 milligram; but (column 3) the sum of the preceding weights is equal to $5 \times 1' - 0.1$ milligram, therefore the 5-gram weight is equal to $5 \times 1' - 0.3$ milligram.

The choice of a small weight as the unit of comparison throws a big error on the larger weights. In order to secure a uniform distribution of the relative errors, the assumption is now made that the sum of all the weights is exactly 100 grams, and the value of the provisional unit, on this assumption, is calculated.

The sum of the weights,

$$\begin{aligned} &100 \times 1' - 11.0 \text{ milligrams} = 100 \text{ grams,} \\ \text{or} \quad &100 \times 1' = 100 \text{ grams} + 11.0 \text{ milligrams,} \\ \text{or} \quad &1' = 1 \text{ gram} + 0.11 \text{ milligram.} \end{aligned}$$

The value of the provisional unit, $1'$, is thus 1 gram + 0.11 milligram.

Now substitute this value for each $1'$ in column 3 of the table on p. 15. The following are the results:—

Nominal value.	Actual value.		Error.
$1'$	$\approx 1 \text{ gram} + 0.11 \text{ mg.}$	$= 1.0001$	+ 0.1 mg.
$1''$	$= 1 \text{ gram} + 0.11 \text{ mg.} - 0.1 \text{ mg.}$	$= 1.0000$	<i>nil.</i>
$1'''$	$= 1 \text{ gram} + 0.11 \text{ mg.} + 0.1 \text{ mg.}$	$= 1.0002$	+ 0.2 mg.
2	$= 2 \text{ grams} + 0.22 \text{ mg.} - 0.1 \text{ mg.}$	$= 2.0001$	+ 0.1 mg.
5	$= 5 \text{ grams} + 0.55 \text{ mg.} - 0.3 \text{ mg.}$	$= 5.0003$	+ 0.3 mg.
$10'$	$= 10 \text{ grams} + 1.1 \text{ mg.} - 0.9 \text{ mg.}$	$= 10.0002$	+ 0.2 mg.
$10''$	$= 10 \text{ grams} + 1.1 \text{ mg.} - 1.1 \text{ mg.}$	$= 10.0000$	<i>nil.</i>
20	$= 20 \text{ grams} + 2.2 \text{ mg.} - 2.5 \text{ mg.}$	$= 19.9997$	- 0.3 mg.
50	$= 50 \text{ grams} + 5.5 \text{ mg.} - 6.1 \text{ mg.}$	$= 49.9994$	- 0.6 mg.
Total 100		$= 100 \text{ gms}$	+ 0.0 mg.

It will be observed that the sum of all the errors is now zero, a necessary consequence of the assumption that the sum of all the weights is equal to 100 grams. The error in the 50-gram piece is now -0.6 milligram, and the minus sign indicates that, when the 50-gram weight is used in a weighing,

0.6 milligram should be *deducted* from the observed weight. It may be noted, however, that in a "difference" weighing, if the same pieces as far as possible are used, the actual error in the result may be nil, or very small, even if the corrections are not applied.

The sum of all the fractions, viz., $0.5 + 0.2 + 0.1' + 0.1'' + 0.05 + 0.02 + 0.01' + 0.01'' + 0.01'''$ (the rider), is next compared with one of the single gram weights. Finally, the fractions themselves are compared with one another and, if more than negligible differences are found, the errors in the individual fractions are computed in the manner already indicated.

If a 1-gram standard weight is available, the 1-gram weight chosen as a provisional unit should be compared with it and the absolute values of the other weights calculated from the data already obtained.

It is convenient to construct a table showing the amount to be added or subtracted when using any combination of weights. Four columns are necessary, showing the corrections, (1) when using 10, 20, . . . 90 grams; (2) when using 1, 2, . . . 9 grams; (3) when using 0.1, 0.2, . . . 0.9 grams; and (4) when using 0.01, 0.02, . . . 0.09 grams.

Modern Balances

The general tendency in the development of balance design has been to produce balances that weigh more rapidly and more precisely. One of the earlier devices was the replacement of the rider by a light chain attached at one end to the balance beam, and at the other to a hook fixed to a block which could slide up and down a graduated vertical column, the movement being controlled from outside the balance-case. According to the position of the block, a greater or smaller proportion of the weight of the chain was carried by the balance beam. The vertical column was so graduated that milligrams and tenths of a milligram could be read off directly from the position of the block, a vernier scale being provided. Most modern rapid-weighing balances are fitted with automatic weight-loading devices for adding weights down to centigram values; milligrams and tenth milligrams are read directly from a graticule fixed to the pointer of the balance. A magnetic or air-damping device is fitted so that the beam comes to rest at the end of the

first swing, and a projection system is attached so that an enlarged image of the graticule is seen on a screen. The sensitiveness of the balance is adjusted so that one division of the graticule scale is equivalent to a tenth milligram, and the sensitiveness is constant for all loads. The most recent development is the so-called "single-pan" balance, in which one arm of the beam carries a fixed permanent load of about 200 grams, and the other arm carries a pan and a set of weights which can be automatically removed or replaced. The zero-point of the balance is set, then the object to be weighed is placed on the pan and weights *removed* from that arm of the balance until equilibrium is restored. The milligrams and tenth milligrams are recorded from a projection scale. The main advantage of this type of balance is the certainty that the sensitiveness will be constant whatever the weight of the object, since the *total* load is constant.

NOTES ON GENERAL APPARATUS

The following notes are intended to form a guide in the selection of suitable sizes and shapes of certain common pieces of apparatus. The special apparatus required for volumetric and for gravimetric analysis is described in Parts II and III respectively.

Wash-bottle.—A 500 to 1000 ml. round flask (Fig. 15, p. 40) is the most convenient size. The jet, which must deliver a fine stream of water, should be within easy reach of the forefinger, in order that only one hand may be necessary to manipulate the wash-bottle (Fig. 16, p. 40). Thick string should be wrapped round the neck of the flask in order to protect the hand when hot water is used.

Beakers.—The most satisfactory beakers for quantitative analysis are made from special resistance glass (*e.g.* Pyrex glass) and are provided with a spout. The spout is not only for convenience in pouring, but it forms an outlet for steam or escaping gas when the beaker is covered with a clock-glass; it prevents the sealing of the beaker with a ring of liquid, portions of which may be projected and lost during boiling. The spout also forms a convenient place at which a stirring-rod may protrude from a covered beaker (Fig. 8, p. 34).

The size of a vessel must be chosen with due regard to the total volume of liquid which it is to contain, *i.e.* neither too large nor too small: for precipitations in gravimetric analysis, 300 ml. and 400 ml. beakers (12 to 14 cm. high) are the most generally useful sizes, and for ordinary titrations 200 ml. and 300 ml. *conical* beakers (Fig. 1).

Flasks.—Conical flasks (200 to 400 ml.) with wide mouths (2.5 cm.) are convenient for many purposes.

Casseroles.—Porcelain casseroles (Fig. 2) are used for the



FIG. 1.



FIG. 2.

same purposes as porcelain basins, and are more convenient to handle.

Funnels.—The most useful sizes are about 5.5 cm. and 7 cm. in diameter. The sides of funnels must be plain, and should enclose an angle of 60° . The stem should be not less than 8 cm. long and about 4 mm. in diameter (internal). Funnels with short, wide stems are unsuitable for filtration purposes. Filtration is rapid in some funnels and slow in others, and the variation in this respect is very marked. It is worth while testing a number of funnels and selecting the best.

Stirring-rods.—Very light rods for use in beakers may be made from glass *tubing*, 4 to 5 mm. in diameter, by carefully sealing *both* ends in the blowpipe flame. Open glass tubes must not be used as stirring-rods. If made from glass rod, the ends should be rounded in the Bunsen or blowpipe flame. A stirring-rod should be suitable in length for the size and type of the vessel in which it is to be used, *e.g.* 2 cm., at most, longer than the diameter of a basin, or about 5 cm. longer than the height of a beaker (Fig. 8, p. 34). If the beaker has no spout and is to be covered with a clock-glass without removing the rod, a shorter rod is required—one that will rest obliquely inside the beaker without touching the

clock-glass. Rubber-tipped rods are used for a special purpose only (see p. 43) and should not be used for stirring solutions.

Boiling-rods.—In order to prevent a boiling liquid from superheating and “bumping,” a boiling-rod may be used.



A boiling-rod is made from a piece of glass tubing which is closed at one end, and sealed *near* the other end, as shown in Fig. 3. The open end must be cut off so as to leave a little cup about 0.5 cm. deep, and this end is immersed in the liquid. When the rod is removed, the liquid in the cup-shaped end must be shaken out and the rod rinsed with a jet of water.

Desiccators.—A desiccator is used (1) to keep hygroscopic substances dry or (2) to effect the actual drying of wet substances. Dehydration in an ordinary desiccator is a comparatively slow process and requires many hours or even days. An evacuated desiccator is more efficient.

Either concentrated sulphuric acid or lumps of fused calcium chloride may be used as the drying agent.

The layer of sulphuric acid should not be more than 0.5 cm. deep, and if the desiccator is in regular use the acid should be renewed occasionally. The ground rim of the desiccator should be greased with vaseline, sparingly used.

When extreme drying conditions are required, phosphorus pentoxide is used. It is advisable to place this in a small dish inside the desiccator to prevent the possibility of cracking when the partially exhausted phosphorus pentoxide is washed out. An efficient drying agent recently introduced is magnesium perchlorate, used either as the trihydrate or as the anhydrous salt, the latter being known as “anhydrone.”

Hot crucibles should never be placed directly on the perforated zinc in a desiccator, but should be placed in suitable stands made of glass or porcelain.

Wire Gauze.—Tinned iron wire gauze, 12.5 cm. square with an asbestos centre, is very durable, and forms a satisfactory and flat support for a beaker or flask that is to be heated.

Paper Mats.—By placing beakers and flasks containing liquid, not directly on the bench top, but on paper mats (10 cm. in diameter) or on pieces of thick blotting-paper, the risk of scratching the glass with sand grains, etc., often the cause of subsequent fracture, is avoided.

Plastic Ware.—Some reagents, for example, hydrofluoric

acid, sodium hydroxide solution and ammonia solution, attack glassware more or less readily. It is convenient to keep such reagents in containers made of polythene, and to use polythene apparatus for measuring and transferring these reagents. Polythene and bakelite beakers and funnels are commercially available; pipettes for the transfer of *small* volumes of liquid can be made from polythene tubing by rotating it about two inches above a quarter-inch micro-bunsen flame until it softens, gently drawing a capillary, allowing it to cool, and then cutting with a sharp knife at the appropriate place. Small rubber teats can be attached to these pipettes if desired.

PREPARATION OF THE SUBSTANCE FOR ANALYSIS

Pure Salts.—The salts of commerce described as analytical reagents are of a definite standard of purity and may be used without special purification, as a rule, for practising typical methods of analysis and for the preparation of standard solutions.

In the case of a salt of doubtful purity, a good specimen can usually be obtained by recrystallisation. Twenty grams or more of the salt are dissolved in the minimum quantity of hot water contained in a beaker. The hot solution is poured through a fluted filter placed in a funnel with a very short stem (1 to 2 cm.), and the clear filtrate is received, with constant stirring, in a porcelain basin which is cooled by placing it in a large dish containing cold water. If much crystallisation is liable to occur during filtration, this may be carried out in a filter funnel heated by steam or electrical means. Alternatively, the filtration of the hot saturated solution may be effected rapidly by suction through a Büchner funnel (Fig. 4), in which a circle of filter paper is placed to cover the perforations. The filtrate is collected in a previously heated filter-flask (Fig. 18, p. 44), and then rapidly poured into a conical flask, which can be cooled in a stream of water while the flask is shaken.

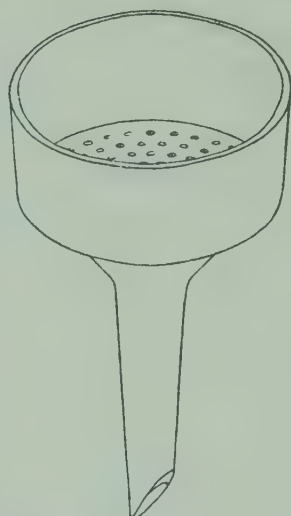


FIG. 4.

The fine crystalline "meal" thus obtained is purer than a product consisting of large crystals formed during slow cooling, as these may enclose some of the mother-liquor. The fine crystals are then separated from the mother-liquor by filtration through a Büchner funnel. The salt is well pressed down in the funnel and the mother-liquor removed as far as possible by means of the filter-pump, washing with a little cold water unless the salt is very soluble. The crystals are pressed between filter paper and then "air-dried" for twelve hours, first by spreading upon filter paper, and then, as paper is itself hygroscopic, on a clock-glass, dust being excluded. Salts which effloresce must be dried as quickly as possible and bottled. Deliquescent salts require special treatment. If the salt contains no water of hydration, it may be dried in a vacuum desiccator; and if it suffers no alteration at 100° or at higher temperatures, it may be dried in the air-oven.

Metals and Alloys.—In the case of the softer metals, pieces suitable for analysis may be cut from the main sample by means of shears, or the metal may be rolled, in a steel rolling-press, into thin ribbon or foil. If this is not practicable, a representative sample should be obtained in the form of borings (by means of a steel drill), which should be taken from a number of different parts, as segregation may have taken place on solidification. If the borings are contaminated with oil, they must be washed with ether and then dried.

Minerals, Rocks, and Ores

Sampling.—If the material is more or less homogeneous, sampling is comparatively simple, since a small picked sample will usually be representative of the whole; whereas, if the material is a bulky heterogeneous mass, such as a consignment of ore or coal, it is by no means an easy matter to obtain a sample that will represent as far as possible the average composition.

Procedure when an Average Sample is required.—The sampling of ores and other commercial products is a matter of great importance, since their market value is based on the results of the analyses of small samples. Full details of the elaborate methods that are often found necessary in commercial

practice cannot be given here, but a general outline of the procedure is as follows :—

- (1) A *large* representative sample is obtained. Any “selection” of pieces different from the average in quality is avoided by taking portions according to some rigid system ; for example, a shovelful is taken from each barrow-load or truck-load.
- (2) The large sample is then ground to a coarse powder and thoroughly mixed, and portions of this are again taken systematically, and the process of reduction in size and quantity repeated until a sample small enough to be sent for analysis is obtained.

The sample received by the analyst would be treated on the following lines :—

Small representative portions for analysis are obtained by spreading the sample on a piece of oil-cloth or tough paper 75 cm. square, and mixing further by lifting and pulling each corner in turn towards the opposite corner. The particles roll over each other, and the lower layers are brought uppermost. The mass is then shaped into the form of a flattened cone, and divided through the centre by two vertical cuts at right angles to each other. Two opposite quarters are rejected, and the remaining quarters are further ground, remixed on the cloth, and again quartered. This process is repeated until finally a sample is obtained, the size of which depends upon the type of analysis required. Even this sample should not be taken as absolutely homogeneous, and therefore in weighing small quantities, portions should be selected from several different parts of the sample.

Procedure when a Picked Sample is required.—If the substance is a mineral, a clean sample as free as possible from adhering gangue should be “selected.” By roughly crushing the mineral, it is often possible to detach any material foreign to the mineral proper. In the case of rocks, a few chips broken from a hand specimen will usually be representative. The picked sample, which should weigh about 10 grams, must be powdered.

Crushing and Grinding.—If the material is hard, it is first broken into coarse powder on a hard steel plate (about 10 cm. square and 4 cm. thick) with a hardened hammer.

Loss of flying fragments is prevented by means of a steel ring (8 cm. in diameter and $2\frac{1}{2}$ cm. high) which is laid on the steel plate, or in some other manner.

A "percussion" mortar (Fig. 5) may be used for crushing small lumps. The mortar consists of three pieces—a block (A), a hollow cylinder (B), and a pestle (C)—all of very hard steel. The selected lumps, one piece at a time, are placed in the cylinder (which fits into a depression in the block) and are crushed by striking the pestle with a hammer three or four times. The crushed material is transferred to a 100-mesh sieve, and sieved. The material that fails to pass the sieve is returned to the mortar for further crushing.

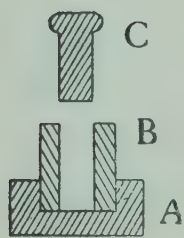


FIG. 5.

This treatment is continued until the whole of the sample will pass a 100-mesh sieve.

In order that the decomposition of the mineral by acids or by fusion with alkali carbonates, etc., may be successfully accomplished, a very fine powder is often essential; on the other hand, prolonged powdering is not always necessary and may even lead to error in the analysis. If the mineral contains ferrous compounds, for example, partial oxidation of the iron may occur during the grinding process. Finely ground powders may also take up an appreciable amount of water from the air, and water of hydration may be expelled from minerals by long-continued grinding. Each mineral or rock demands individual treatment in this respect and it is impossible to give general rules. Usually, however, crushing to pass a 100-mesh sieve will suffice; further grinding, if necessary, is best done with an agate mortar and pestle, taking small quantities at a time.

WEIGHING THE SUBSTANCE

The accuracy required in this operation depends on the amount of substance that is to be weighed and on the percentage of the constituent that is to be determined. Suppose a 0.3 per cent. carbon steel is being analysed for carbon by combustion in oxygen and measurement of the weight of carbon dioxide produced, and suppose the sample weight is about 3 grams. The carbon dioxide produced will weigh about 33 milligrams,

and it can be weighed with a precision of about 10 parts per 1000. That is to say, the sample weight would need to be in error by 0.1 gram to alter the carbon percentage by 0.01, or in error by 10 milligrams to make the smallest perceptible difference in the weight of carbon dioxide. Clearly, it is necessary to weigh the sample only to the nearest centigram in this case. On the other hand, in the analysis of sodium chloride for its chlorine content, by precipitation and weighing of silver chloride, it would be necessary to weigh 1 gram of sample accurately to 0.1 milligram. The desired accuracy of weighing can readily be assessed from a knowledge of the circumstances. If a modern rapid-weighing balance is available, it is just as quick to weigh to 0.1 milligram as to the nearest centigram, but if it is necessary to weigh by swings, much time can often be saved by weighing the sample with an accuracy sufficient for the particular determination (*cf.* p. 8). The weight of substance is always found by "difference," and is usually determined in one of the following ways:—

- (1) Place 3 to 4 grams of the substance, or a larger quantity if necessary, in a clean, dry weighing-bottle (Fig. 6), and weigh the bottle and its contents. Shake from

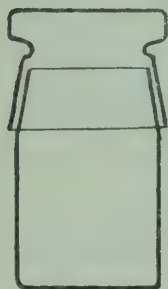


FIG. 6.

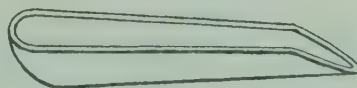


FIG. 7.—Scoop for Weighing.

the bottle (into the vessel in which the next operation is to take place) a quantity that, judged by the eye, is approximately equal to the amount prescribed, taking care that none of the substance is lost in the process. Weigh the bottle with the remaining substance again. The difference between the two weighings gives the weight of substance taken. It does not matter if the weight is a little more, or a little less, than that desired. If it is considerably less, a further quantity may be shaken out and the second weighing repeated. If it is considerably more, an attempt should be made to return part of the

- substance to the weighing-bottle, but the whole operation should be begun afresh. The bottle should be handled as little as possible between the weighings.
- (2) Weigh a glass scoop. (A watch-glass may be used instead.) With the forceps lift the scoop off the balance-pan, and, with a spatula, place upon it what is judged to be the right quantity of the substance. Reweigh the vessel and contents. (It saves time in subsequent weighings if the weight of the empty vessel is marked upon it by means of etching ink or as described on p. 59.)
 - (3) If the vessel in which the substance is to be dissolved, heated, etc., is comparatively small and light, such as a crucible, weigh the substance directly in the tared vessel.

The first method should be used if several portions of the substance have to be weighed, the separate quantities being successively shaken out of the weighing-bottle which is weighed after each operation.

Liquids and volatile or hygroscopic solids *must* be weighed in a stoppered weighing-bottle.

Vessels that are to be weighed should not be placed directly on the working-bench but on a sheet of clean paper.

The vessels used as containers should be as small as possible.

ERROR IN QUANTITATIVE WORK

All quantitative determinations are liable to error, however carefully carried out, and at best they only approximate to the true value of the quantity sought. In considering experimental error, a distinction should be drawn between precision and accuracy. When analytical work is carried out with a high degree of precision, the results obtained in a series of determinations of any constituent agree closely amongst themselves. It does not, however, follow that they approximate to the true value, as some constant error may be affecting all the determinations. On the other hand, when the work has been carried out with a high degree of accuracy, the results will be closely grouped round the true value, some below and some above. By taking the mean of such determinations a close approach to the true value will be attained.

Errors are of two kinds : (1) Those which are unavoidable. A series of determinations carried out by the same person in as nearly as possible the same way shows slight discrepancies. The larger the number of determinations, the smaller will be the deviation of their mean from the true value. (2) Those which are avoidable, arising from want of care in carrying out the work, including the use of unsuitable or faulty apparatus, or from the lack of manipulative skill on the part of the worker, or from errors associated with the method of the analysis employed. These last can often be partially eliminated or allowed for. For instance (a) errors from the solubility of a precipitate may be calculated, or reduced by the common ion effect ; (b) errors from adsorption of some soluble substance on the precipitate may be prevented by previous removal of such a substance ; (c) errors from the formation of a colloidal solution during the washing of a precipitate can usually be prevented by washing with a solution of a suitable electrolyte ; (d) errors from the variation in the composition of a precipitate under slightly different conditions of formation can be reduced by controlling such conditions as carefully as possible. Errors can often be allowed for by carrying out a determination under the same conditions using a known amount of the substance being determined, which is as nearly as possible equal to that in the sample being analysed. This is known as *check* or *control* analysis. In certain cases where impurities in the reagents used might give rise to error, a *blank* determination is made under similar conditions, but the substance which is to be determined in the unknown sample is omitted in this blank test.

Amount of Substance required for Analysis, and Limits of Allowable Error

After the experimental errors have been reduced to a minimum, the relative error in the final result depends on the amount of substance taken for analysis. It is important to realise that it is not so much the absolute value of an error that is important as its magnitude relative to the quantity being determined. An absolute error of 0.04 per cent. is far more serious in the determination of a component that is present to the extent of 0.1 per cent. than in the determination of one present to the extent of 10 per cent. In calculations it is

convenient to express the relative error in parts per thousand to avoid confusion with the percentage of constituents. If limits of error are quoted in the result, however, they must be expressed in terms of the percentage of constituent present.

In volumetric analysis the error in the measurement of the volume of liquid delivered by the burette varies from 0.00 to 0.05 ml. Taking the higher limit, and assuming that only 5 ml. of the solution in the burette are used, the error is 10 parts per 1000; if 25 ml. had been required, the same error in the measurement would have represented a relative error of only 2 parts per 1000. As a general rule the amounts taken should be such that from 20 to 30 ml. of the solution in the burette are required for each titration. The total error in volumetric analysis by an accurate method should not exceed 3 parts per 1000.

In simple gravimetric analysis, the amount of substance taken should be sufficient to give from 0.2 to 0.5 gram of precipitate in the final weighing. The unavoidable error arising in the course of the work should not, in general, exceed 1 milligram. One milligram represents a relative error of 10 parts per 1000 if the weight of the whole precipitate is 100 milligrams, but only 2 parts per 1000 if the precipitate weighs 500 milligrams. The amount of substance taken, therefore, should not be too small. With bulky, flocculent precipitates, like ferric hydroxide, which are difficult to filter and wash, an amount to give about 0.2 gram of precipitate is desirable, whereas with precipitates like silver chloride or barium sulphate, 0.5 gram, or even 1 gram if need be, is easily dealt with.

In the complete analysis of a complex substance, such as a rock, in which many constituents are present in widely varying proportions, no general rules can be given here; an amount varying from 0.5 to 1 gram is usually suitable.

Expression of Results

Care should be taken in expressing the final result of an analysis to avoid giving more significant figures than are justified by the known accuracy of the data. The significant figures of a number are those which begin with a figure other than a nought. The accepted practice is to include in the final result no more significant figures than the first doubtful

one. For example, the quantity 3.148 grams means that the weight is nearer 3.148 than 3.147 or 3.149 grams. The expression 4.8600 has five significant figures, but a single nought before the decimal point and one or more noughts just after it do not count as significant figures as they are only used to fix the decimal place, and would disappear if different units were used in expressing the quantity, *e.g.* 0.0079 gram could be written 7.9 milligrams. If the figure 6 is the first doubtful one in the expression 25,600 grams, this quantity should be written 25.6 kilograms or 2.56×10^4 grams.

No result should be expressed to a greater number of figures than the number of significant figures in any quantity entering into the calculation. For instance, in calculating the parts per hundred thousand of chlorine in a sample of water, if 5.3 ml. of N/10 silver nitrate were required in titrating 200 ml. of the sample, the calculation should be shown as $5.3 \times 0.00355 \times 100,000 / 200 = 9.4$ parts of chlorine per 100,000. The result should not be expressed beyond two significant figures, since the volume of silver nitrate in this type of titration cannot be determined to more than two significant figures. There is no advantage in using the figure 0.0035457 gram for the weight of chlorine equivalent to 1 ml. of N/10 silver nitrate, and calculations may often be simplified by rounding off the figures in the more accurately known quantities. The rounding off must not be carried too far, however. It is usual to retain in each factor in calculations one more significant figure than is necessary and then round off the final result. If a calculating machine is used there is little advantage to be gained by approximating factors.

It is not possible to form an estimate of the total error in any particular determination, since the individual errors arising from chemical processes and manipulative faults cannot be assessed. These errors may reinforce one another or partially cancel; in either case the total effect will vary from one determination to another. It is, however, possible to form an estimate of the observational errors arising from the use of instruments such as balances, burettes, etc. For this purpose it is necessary to find the *standard deviation* of a single observation.

If the same object is repeatedly and independently weighed on the same balance against the same weights, it will be found

that the observed weight will not be constant, but will fluctuate over a small range of weights, the range usually being of the order of one or two tenths of a milligram. This fluctuation is inherent in the method of weighing and is not under the control of the observer. If the frequency with which individual weights occur is plotted against the weights it will be found that the distribution forms a fairly symmetrical bell-shaped curve. That is, the most frequently observed weights are very close to the mean weight, and the extreme weights occur relatively infrequently. The distribution should be the *normal* or *Gaussian distribution*, which is the curve of the equation :

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-m)^2}{2\sigma^2}}$$

where y is the probability density of the observed variable x , m is the true value, σ is the standard deviation, and π and e have their usual mathematical meaning. The standard deviation σ is the true standard deviation ; in practice this quantity is not known, but an estimate of it, the estimated standard deviation s , is made by means of the equation :

$$s = \sqrt{\frac{\sum(x-\bar{x})^2}{(n-1)}}$$

where n is the number of observations, and \bar{x} is the arithmetic mean of the observations. At least ten independent observations should be made for the determination of s . The importance of the standard deviation is that about 95 per cent. of the observed values will lie in the range $\bar{x} \pm 2s$, and about 99 per cent. in the range $\bar{x} \pm 2.6s$. That is, if the standard deviation for a given load on the balance is known, and an object of that weight is weighed once, in nineteen cases out of twenty the observed weight will be in error by not more than twice the standard deviation.

Once the standard deviation of a single weighing has been determined, it is easy to calculate the limits of observational error. Suppose a sample of brass is being analysed electrolytically for copper, and suppose that the balance has a standard deviation of s mg. at the loads used. In weighing the sample suppose there is an error of x mg. in the first weighing, and y mg. in the second. Then we implicitly suppose that both x and y

are independent random variables which are normally distributed, and have zero mean and a standard deviation s mg. The error in the weight of sample is $x-y$ mg. This error is again a normally distributed random variable with zero mean, but now it has a standard deviation $(s^2+s^2)^{\frac{1}{2}} = s\sqrt{2}$ mg. (In statistical language we have Variance $(x-y) = \text{Variance } (x) + \text{Variance } (y)$: standard deviation $= (\text{Variance})^{\frac{1}{2}}$). Similar reasoning will apply to the standard deviation of the weight of copper deposited. The percentage of copper is then calculated from the ratio of the weight of copper and weight of sample. Suppose these weights to be X mg. and Y mg. respectively (we are supposing that X and Y are normally distributed random variables with means the true weight of copper, \bar{X} , and the true weight of sample, \bar{Y} , both with standard deviation $s\sqrt{2}$). The observed percentage of copper is hence $100X/Y$. To the first order :

$$\text{Variance } 100X/Y = 10^4 \left[\frac{\text{Variance } X}{\bar{Y}^2} + \frac{\bar{X}^2 \text{Variance } Y}{\bar{Y}^4} \right].$$

Taking the case where $s = 0.1$ mg. and 60 per cent. of copper is determined in about 1 gram of sample, we find that the standard deviation of the observed percentage of copper is 0.016 per cent. That is, in 99 per cent. of determinations of copper in that sample of brass under these conditions the observational error will not exceed 0.04 per cent. of copper. There are then two methods of reporting the percentage of copper. Either it can be reported in full to two decimal places together with a quotation of the estimated standard deviation, or it can be rounded off to the first decimal place so that the estimated error is implied by the number of significant figures quoted.

It is necessary to modify the reasoning given above, in the cases where the final weighing form is different from the constituent sought, so that a conversion factor is necessary in the calculations, and in the cases where the final weighing is made to "constant weight." In the first case, if W is the weight of the precipitate, and A is the conversion factor, so that $X = AW$, then :

$$\begin{aligned} \bar{X} &= A\bar{W}, \\ \text{Variance } X &= A^2 \cdot \text{Variance } W. \end{aligned}$$

In the second case, heatings and weighings are repeated until

two consecutive observations agree within some previously decided limit, say k mg., the observed weight being taken as the mean of the last two observations. Obviously k should not be less than the error reasonably to be expected in a single weighing.

If indeed true constant weight has been reached, the last two weighings are independent observations of the same quantity, and the observed mean has, therefore, standard deviation $s/\sqrt{2}$, and mean the true weight. This will reduce the standard deviation of X in the example considered, but will make only a negligible difference to the limits of observational error already quoted.

In the case of volumetric determinations it is possible to estimate the observational error in the burette readings, and the error involved in the control of addition of reagent, which determines the error involved in determining the end-point. If the smallest amount of reagent that can be added conveniently is 0.03 ml., then an end-point that occurs within such an addition may be in error by almost the whole of the increment.

Suppose the amount of iron in an ore is being determined by reduction of the iron to the ferrous state and titration of the ferrous iron with ceric sulphate. Then the observational error may be calculated as follows.

In order to estimate the standard deviation of the volume of reagent added from the burette we need to consider the errors in reading the burette at the beginning and the end of the titration, and the error arising from the actual position of the end-point within the last increment of titrant. Let us suppose that each reading of the burette is accurate to ± 0.01 ml., and that the smallest drop of titrant that can conveniently be added is 0.03 ml. The error in the amount of titrant needed lies between -0.02 and $+0.05$ ml. The standard deviation will, then, be of the order of 0.02 ml. (We are assuming a normal distribution; there is a good case for supposing the distribution to be rectangular, but this distinction would make but little difference to the standard deviation.) We shall not consider such errors as drainage in the burette during the titration.

Apart from errors in the use of the burette, there is likely to be an error in the standardisation of the titrant. We may suppose this to be about 1 part per 1000. One millilitre of

0.1 N ceric sulphate is equivalent to 5.585 mg. of iron, so that this error in standardisation would be equivalent to an error of about 0.0056 mg. of iron per ml. of titrant; the standard deviation is then about 0.002 mg./ml. Let x ml. be the amount of titrant used, and y mg./ml. be the iron equivalent of the titrant. Then the observed amount of iron is xy mg., and we have to the first order, using bars to denote means as before:

$$\text{Variance } (xy) = \bar{y}^2 \cdot \text{Variance } x + \bar{x}^2 \cdot \text{Variance } y.$$

If a gram of sample containing about 12 per cent. of iron is being analysed, and y is about 5.6 mg./ml. then x will be about 20 ml., and we find that the variance in the amount of iron is 1.4×10^{-2} (mg.)². That is, the standard deviation of the amount of iron is 0.12 mg., and the standard deviation of the percentage of iron is approximately 0.01 per cent. That is to say, the 99 per cent. limits of error are ± 0.026 per cent.

In some methods of analysis a number of constituents are precipitated and weighed together, and the amount of one of them is determined by finding the combined weight of all the others and subtracting it from the total weight. This is an *indirect* method of analysis. In such a determination the variance of the amount of substance so found will be the sum of the variances of the contributing factors. Obviously the observational error in an indirect method is likely to be rather larger than that in a direct method.

From the foregoing it is evident that the 99 per cent. limit of observational error amounts, in cases of major constituents, to several units in the second decimal place of percentage. Chemical or manipulative errors, which we have not considered, may considerably increase the actual error. The results should be quoted either in full, *i.e.* giving two decimal places, together with the estimated standard deviation, or else to such a number of decimal places that variation within the 99 per cent. limits of error causes a variation of at most one unit in the last figure quoted. It will usually be found that no more than three significant figures can be justified in the reported percentage of any constituent.

It must be remembered that the normal distribution of errors can be expected to apply only to observational errors. The distribution of the results of analytical determinations is seldom normal. Calculation of the observational error is intended, not

to give an estimate of the accuracy of a determination, but to give a guide to the precision to be expected in the absence of chemical or manipulative errors.

DISSOLUTION OF THE SUBSTANCE

Provided the nature of the substance and solvent allows, the substance is brought into solution in the vessel in which the next operation is to take place. As a rule, either a beaker, a flask, or a porcelain basin is suitable.

With regard to the choice of vessels for quantitative analysis, it should be remarked that the solvent action on glass of water, acids, and more especially alkaline solutions, is considerable, and in accurate work it cannot be neglected. The amount dissolved depends on the nature of the glass, and increases with the temperature and with the length of time the glass and liquid are in contact. It is considerably less in the case of glass vessels that have been in use for some time. Porcelain and borosilicate glass resist the action of solvents much better than ordinary glass, and should be used as far as possible in

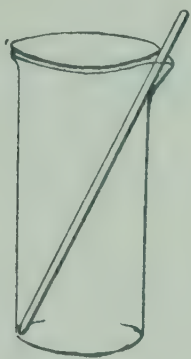


FIG. 8.



FIG. 9.



FIG. 10.

preference to the latter. Plastic vessels should be used for work involving the use of hydrofluoric acid, or in cases where it is necessary to avoid contaminating the solution with silica or alkali metal ions.

If precipitation is to follow dissolution, the weighed substance is brought into solution in a beaker. Dissolution may be promoted, if necessary, by heating the beaker (supported on wire gauze) with a Bunsen flame, or by warming on a steam-bath. If actual boiling is required, or if gases are evolved, loss of substance by spirting or spray is prevented by covering the beaker with a clock-glass (Fig. 8). The clock-glass should be, at most, half an inch larger than the mouth of the beaker, and,

in order to provide an outlet for steam or escaping gas, the beaker should have a spout. If evaporation is to follow dissolution a porcelain basin is used, also covered with a clock-glass of suitable size. In the case of a flask, loss of substance is prevented by placing a small funnel in the mouth of the flask (Fig. 9), or by clamping the flask in a sloping position. A flask should be used, as a rule, if prolonged heating with volatile acids is necessary, and in this case a glass bulb may be placed in the mouth of the flask (Fig. 10).

After dissolution is complete, or decomposition ended, the cover of the vessel must always be rinsed with a jet of water from the wash-bottle, and the washings added to the solution.

EVAPORATION

In this operation three points demand special attention, viz. :—

- (1) No loss of substance must occur in the process.
- (2) It should take place as rapidly as possible—with due regard to point 1.
- (3) Contamination from without must be guarded against.

Loss of substance is prevented by evaporating on the steam-bath, thus avoiding actual boiling of the liquid. As a rule, the process should be conducted in a porcelain basin, not more than two-thirds filled; in a beaker evaporation is slow. Dust, etc., is excluded by placing over the basin a clock-glass, of larger diameter than the basin, supported, *convex side upwards*. This may be held in a clamp, or rest upon a glass tripod made for the purpose. A better device which conveys vapour away more rapidly, and prevents any condensed liquid dropping on to the water-bath, is shown in Fig. 11.

The rate at which evaporation proceeds depends on the continuous removal of the vapour over the surface of the liquid by means of a current of air, and the operation should therefore be conducted in a good draught. A large excess of steam must be carefully avoided.

It is sometimes necessary to conduct evaporation on a steam-bath in such a manner as to protect the contents of the basin from contamination with impurities, such as sulphur dioxide

(from coal-gas flames), ammonia, etc., in the laboratory atmosphere. For this purpose the arrangement shown in Fig. 12 is both simple and efficient. The hemispherical condensing cover may be of glass (an inverted glass basin), or, better, of thin copper. One half of a cistern "ball-cock" float, 15 to 20 cm. in diameter, makes a satisfactory cover and is easily obtainable. The glass or copper cover is cooled by a stream of tap water, and an external source of steam is used. Evaporation by this method is rapid and, on this account, the arrangement may be used in place of the ordinary plan if a good draught is not available.

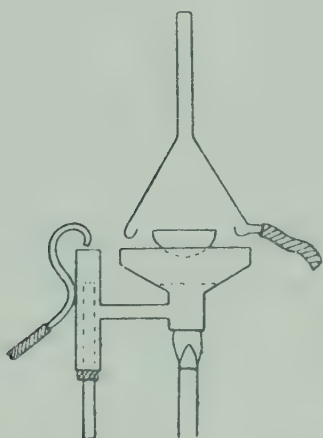


FIG. 11.

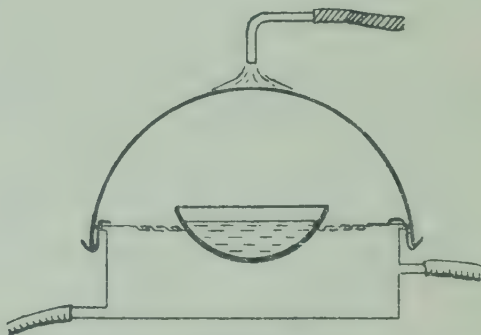


FIG. 12.

Evaporation at the boiling-point may be conducted in a flask, supported obliquely and only half filled. This method is also useful if effervescence from the escape of gas occurs on heating.

A modern method of evaporating liquids is to suspend an electrically heated unit *above* the surface of the liquid. The radiated heat produces evaporation without the accompaniment of bumping or creeping of separated solids.

Evaporation may be hastened by allowing a *slow* stream of air from a capillary tube to impinge on the surface of the heated liquid. The air stream should be just strong enough to dimple the surface of the liquid and no more. This method is particularly useful for the rapid evaporation of small volumes of liquid.

Electrically heated baths are also used for the evaporation and distillation of inflammable liquids. Gas or electrically heated thick metal plates are useful for evaporation purposes, the temperature gradient being made use of for varying the speed of evaporation.

Evaporation of Sulphuric Acid.—The evaporation in a platinum crucible of a liquid of high boiling-point, such as concentrated sulphuric acid, is conducted with a free flame.

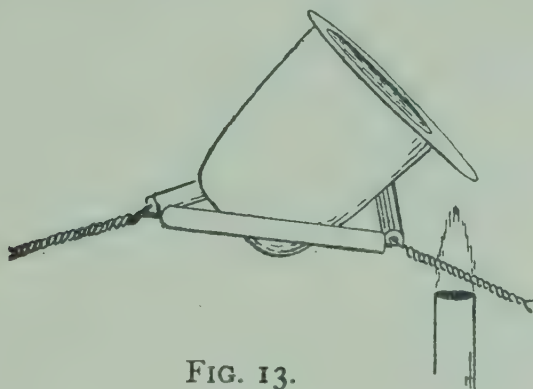


FIG. 13.

In order to avoid loss by spirting and to prevent the liquid from creeping up the side and over the rim, the covered crucible is supported obliquely on a pipe-clay triangle, and the tip of the lid is heated with a small flame (Fig. 13). As the evaporation proceeds the flame may be brought under the rim of the crucible, but care must be taken that the heating is not too rapid.

Another arrangement is to place the crucible within a capacious iron, nickel, or porcelain crucible fitted with an asbestos ring or an appropriate triangle of iron wire wrapped with platinum foil (Fig. 44, p. 237). The outer crucible, without a cover, is heated over a moderately low flame and forms a hot air-bath which ensures uniform heating of the platinum crucible within.

A useful form of air-bath is shown in Fig. 14. It can easily be made in the laboratory workshop from sheet iron or nickel. The joint is riveted and the base B is secured to A by bending the notched edges over one another. A convenient size is 7 cm. high, 7 cm. wide at the top, and 5 cm. at the bottom.

A cheap form of this air-bath is readily made from tin cans, but careful watch must be kept for signs of the bottom burning through. The life of the tin can be lengthened by using the severed lid to make a double bottom in the air-bath.

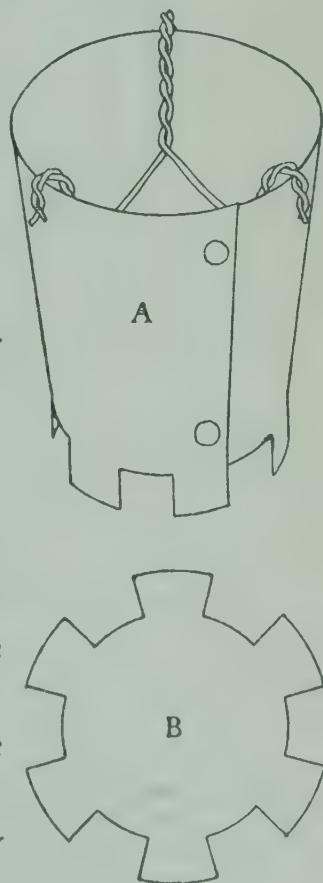


FIG. 14.

PRECIPITATION

This is generally conducted in beakers. Conical flasks are sometimes preferable, but round flasks are unsuitable. Resistance-glass or porcelain vessels should be used in preference to ordinary glass vessels for precipitations with alkali hydroxides and carbonates and with ammonia. The following general considerations regarding precipitation in quantitative analysis may be noted :—

- (1) The precipitate must be of known composition, or must be capable of conversion into a substance of known composition.
- (2) The precipitation must, of course, be as complete as possible, and the precipitate must be in such a condition that it can be filtered and washed in reasonable time.

By choosing suitable conditions under which the precipitation takes place, the character of the precipitate can be controlled to a considerable extent. By avoiding a high degree of supersaturation, the number of primary particles can be kept relatively small ; and this enables them to grow to dimensions which ensure easy filtration. If concentrated solutions of the precipitants are rapidly mixed, a very large number of minute particles separate at once, with the result that a colloidal solution may be produced.

The aim should be to begin the precipitation under conditions of maximum solubility, and gradually to change the conditions so as to decrease the solubility. These conditions can often be attained by suitably adjusting the hydrogen ion concentration, by selecting a suitable temperature for precipitation (most precipitates being more soluble at higher temperatures), and by the gradual addition of one precipitant to a much diluted solution of the other.

A low degree of supersaturation can also be attained by slowly running solutions of both precipitants into water with continuous stirring.

The conditions are finally altered to bring about as complete precipitation as possible, and in such a manner that the particles are allowed to grow in size. For example, in the case of calcium oxalate, if the precipitation is brought about in an ammoniacal

solution, a fine precipitate, difficult to filter, is obtained. If ammonium oxalate, however, is added to a solution slightly acidified with hydrochloric acid, gradual addition of ammonium hydroxide to the boiling solution then produces a precipitate in granular form.

In most cases it is advisable to allow the precipitate to stand some hours before filtering. This not only causes more complete precipitation, but enables the large crystals to grow at the expense of the smaller ones. Moreover, it has been established that aged precipitates are less contaminated by adsorbed ions than those which have just been precipitated.

- (3) The precipitate must be free from contamination with other substances.

In spite of all precautions to prevent it, partial precipitation of small amounts of one or more other substances in addition sometimes occurs. In such cases it is often possible to effect a more or less complete separation by redissolving the precipitate after filtration, and precipitating a second time. As a rule, a slight excess of the reagent must be added; a large excess is, however, generally prejudicial, and is a common source of error. The reagent should be added carefully, a little at a time, until, after allowing the precipitate to settle, it is seen that another drop causes no further precipitation.

It is claimed that readily filterable precipitates, free from contamination by adsorption or occlusion, are obtained by the so-called method of precipitation from homogeneous solution. In this method the precipitating ion is produced *in situ* by such means as hydrolysis or electrolysis; local concentrations of reagent are avoided. Examples are the precipitation of calcium as the oxalate by hydrolysis of ethyl oxalate, and the precipitation of hydroxides or hydroxyquinolates by raising the pH of the solution by hydrolysis of urea.

FILTRATION

In quantitative analysis, filtration must be conducted with much greater care than is sometimes given to the operation in qualitative analysis. The more important rules to be observed are the following :—

- (1) The *size* of the filter depends, not on the volume of the liquid, but on the bulk of the precipitate to be

separated. The precipitate must not more than half-fill the filter. As a rule, a filter paper 9 cm. in diameter is large enough, but for bulky precipitates an 11-cm. paper is required.¹

- (2) The filter paper when folded must be somewhat smaller than the funnel, *e.g.* a 9-cm. paper requires a funnel 5.5 cm. in diameter.
- (3) It is most important that the folded paper should fit the funnel properly. If the funnel angle is not exactly 60°, the paper must be folded with a certain amount of overlap at the second fold so that one cone is larger than the other. In this way a cone of the appropriate size can be obtained. The paper is then held in place in the dry funnel, and, after wetting with water, is well pressed into contact with the funnel wall, especially round the top. This will prevent the entrance of air, and if the stem of the funnel once fills with liquid it will remain full, and the slight suction will effect more rapid filtration.
- (4) If possible, liquids should be filtered hot.
- (5) The underside of the rim of the beaker containing the precipitate should be rubbed at one place with an almost invisible trace of melted rubber² or vaseline and at this place the liquid should be poured down the stirring-rod into the filter, directing the liquid against the side of the filter and not into the apex (Fig. 15). The level of the liquid must not approach nearer than 0.5 cm. to the edge of the paper.
- (6) In order to prevent loss by splashing, the stem of the funnel must rest against the side of the receiving vessel.

¹ A special quality of filter paper which has been extracted with hydrochloric and hydrofluoric acids—so-called “ashless” paper—must be used in quantitative analysis. The ash of a single small filter weighs about 0.1 mg., and is negligible. Several varieties of “ashless” filter papers are made; for flocculent precipitates, like ferric hydroxide, an open texture paper which filters very quickly is desirable, whereas a paper of closer texture is usually required for fine precipitates like barium sulphate or calcium oxalate.

² Obtained by heating the end of a scrap of rubber tubing in a flame.

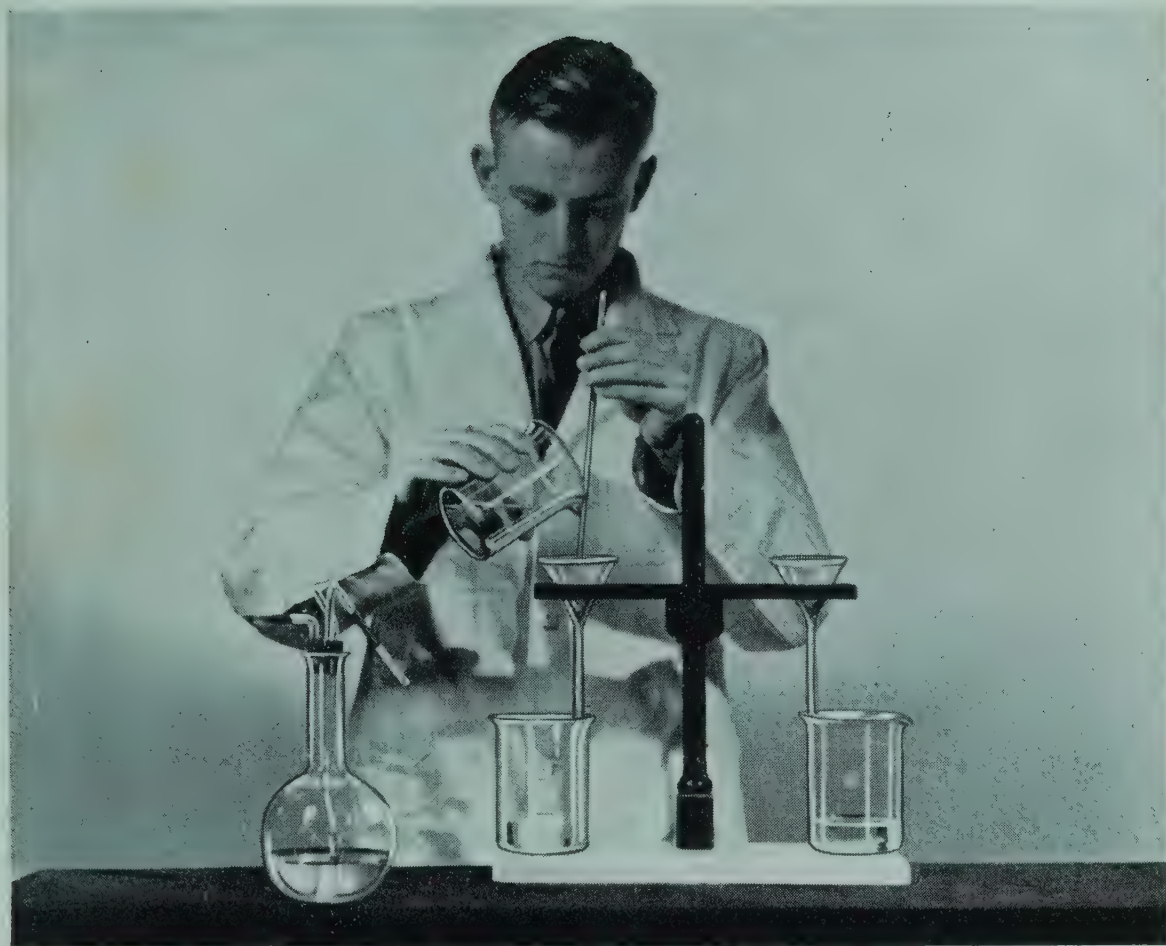


FIG. 15.—Filtration and Washing by Decantation.



FIG. 16.—Transferring the Precipitate to the Filter.

Washing of Precipitates.—In washing precipitates the aim should be to free the precipitate from dissolved substances with the minimum amount of the washing liquid, in order to reduce loss of the precipitate by solution, and to avoid obtaining too large a volume of filtrate if this should be required later. The washing liquid should be chosen so that it has a minimum solvent effect on the precipitate, and does not peptise it even after electrolytes have been washed out. If the precipitate is to be weighed either after drying at a suitable temperature or after ignition, the final washing liquid must not leave a weighable residue, nor must it cause any volatilisation of the precipitate if this is to be ignited, *e.g.* it is better to use a solution of ammonium nitrate than ammonium chloride in washing ferric hydroxide, since some ferric chloride might be formed and volatilised in the latter case.

To fulfil these requirements the washing liquid must be chosen in accordance with the properties of the particular precipitate being treated. Water alone may be satisfactory in many cases, but when electrolytes have been almost washed out of the precipitate there is often a tendency for the formation of a colloidal solution which passes through the filter. This effect is prevented by the use of a solution of an electrolyte such as ammonium chloride or nitrate, which leaves no residue on ignition, but neither could be used as the final washing liquid when the precipitate was to be weighed after drying only. In the latter case an organic solvent is usually employed as the final washing liquid, *e.g.* acetone or alcohol followed by ether. To reduce the solubility of the precipitate in the washing liquid, a solution having an ion in common with one in the precipitate is often employed. For instance, in determining lead as sulphate, the precipitate is washed at first with normal sulphuric acid, in which it is almost insoluble. The solution having the common ion must, however, not be too concentrated in case there is a tendency to form a complex ion which would have the effect of greatly increasing the solubility of the precipitate. A washing liquid which at first sight would appear to be ideal is a saturated solution of the precipitate itself. Theoretically, however, this might lead to obtaining high results, because if the saturated solution is used before first washing out excess of the precipitant the latter would tend to precipitate some solid from the saturated solution used for

washing. Actually in the case of very sparingly soluble precipitates this would not introduce any serious error. For instance in the case of calcium oxalate, the solubility is approximately 6 mg. per litre of water at 18°. If 25 ml. of the saturated solution was used in washing the first time by decantation, and if the excess of ammonium oxalate present in the precipitate caused complete precipitation of the calcium oxalate in the 25 ml. of solution (which would certainly not be the case even on long standing) this would only amount to $\frac{6}{40} = 0.15$ mg. During the subsequent washings still less would separate since the concentration of the ammonium oxalate would be much reduced.

If there is no marked increase in solubility, considerable time may be saved by washing with a hot liquid, since hot liquids filter much more rapidly than cold ones.

Completion of the washing process should always be ascertained by collecting a few drops of the filtrate in a test tube, and testing for an ion such as chloride, if this was present during precipitation, but not contained in the washing liquid. Excessive washing must be avoided, as this would increase losses due to solubility.

Before filtration is begun the precipitate should be allowed to settle; then, without disturbing the precipitate, as much as possible of the clear liquid should be poured into the filter.

If the precipitate settles without long standing, it is much more satisfactory to wash it several times by "decantation" than to transfer it at once to the filter. This is carried out as follows:—After the supernatant liquid has been poured through the filter, add 25 to 60 ml. of the washing liquid and stir thoroughly (the former volume being sufficient for a precipitate which settles to a compact mass). Allow the precipitate to settle again, and once more decant the clear liquid into the filter; repeat the process two or three times. Washing by decantation ensures that all portions of the precipitate come into intimate contact with the washing liquid, which is not the case if washing is carried out on the filter. This applies particularly to gelatinous precipitates, in which crevices and channels are formed, and the washing liquid does not reach portions of the precipitate between these channels. Washing by decantation tends to give bulky filtrates if the

precipitate does not settle well, but in most cases it results in more satisfactory washing than can be attained on the filter alone. It may usually be omitted if the precipitate is very small.

In order to reduce the total volume of washing liquid as far as possible, the following considerations should be borne in mind. Repeated washing with small volumes of liquid is much more effective than the use of the same total volume applied in one or two stages. Another important factor is that the liquid added each time to the filter should be allowed to drain through as completely as possible before adding the next lot. These points may be made clearer by a particular case. Suppose that at each washing the precipitate retains 3 ml. of liquid, and that 27 ml. of washing liquid are added each time, the concentration of the dissolved impurities will be reduced at each stage by $1/10$ of their previous value, provided that the precipitate is merely mechanically contaminated and has not adsorbed dissolved substances. Therefore, after four such stages of washing the concentration of the dissolved substances will have been reduced to $1/10,000$ of their original value. If the total 108 ml. of washing liquid had been used in one operation, the concentration of the dissolved substances left in the precipitate would only have been reduced to $3/111$ or $1/37$ of the original. If, on the other hand, four stages of washing were carried out, but in this case leaving 6 ml. with the precipitate each time, this would leave the precipitate with a concentration of dissolved substances of $\left(\frac{6}{33}\right)^4 = \frac{1}{915}$ of their original value, showing that the washing is much less complete than in the previous case of four stages of washing when the precipitate was more effectively drained.

After washing by decantation, transfer the precipitate to the filter by means of a jet of water from the wash-bottle in the manner shown in Fig. 16. Remove any precipitate adhering to the side of the beaker by means of a stirring-rod tipped with a piece of *black* rubber tubing, 2 cm. long.¹

Wash the precipitate on the filter, bearing in mind the instructions above, and taking care to wash the margin of the

¹ Short rubber tubes, closed at one end, are obtainable for this purpose. Rubber-tipped rods should not be used as stirring-rods and should not be allowed to remain in solutions.

filter paper each time. Be careful not to use so strong a jet of water, or to direct it in such a way, that portions of the precipitate are projected out of the filter. Towards the end of the process endeavour to collect the precipitate as far as possible in the apex of the filter.

Never put anything but distilled water in the wash-bottle.

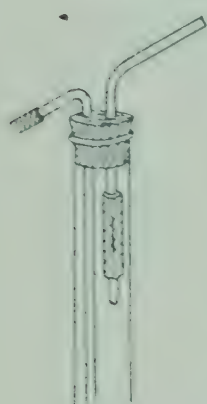


FIG. 17.

Separate small wash-bottles (300 ml.) should be used for ammonia, hydrogen sulphide, alcohol, etc. In order to prevent the backflow of ammonia, etc., to the mouth, a valve may be used. To make the valve, a slit (1 cm.) is cleanly cut in a piece of narrow rubber tubing (3 cm.). One end of the rubber tube is closed with a plug of glass rod, and the valve is then attached to the blow-tube inside the wash-bottle (Fig. 17).

Use of the Filter-Pump.—Accelerated filtration, by means of the filter-pump, is frequently advantageous, especially in the case of bulky, gelatinous, or slimy precipitates like aluminium or chromic hydroxides, or zinc sulphide. The platinum cone which is used to support the filter paper must be well made and in good condition; a bad cone with rough edges is often itself the cause of rupture of the filter paper. In place of a platinum cone, one of toughened paper may be used. Gentle suction only should be used,¹ and the suction should be interrupted as soon as all the liquid has passed through. To effect this most simply without stopping the pump, the latter is connected to the filter-flask through a T-piece, one limb of which is closed by a piece of rubber tubing and clip (Fig. 18). When necessary, the clip is opened to admit air. If any cracks or channels form in a bulky precipitate (the result of continuing suction after all the liquid has passed through), close them carefully with a jet of water or with a glass rod.

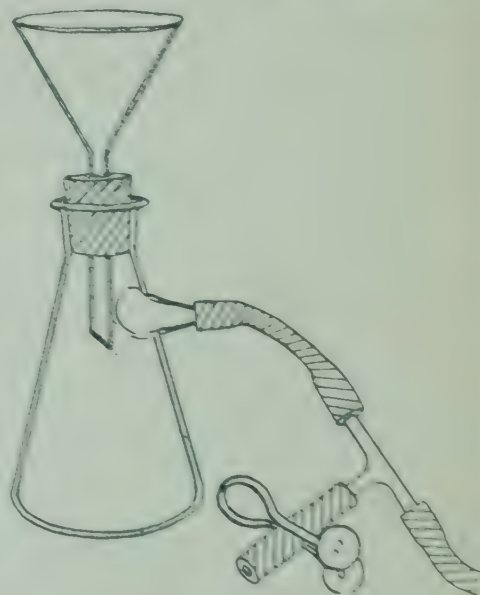


FIG. 18.

Instead of the filter-pump, it is often more convenient

¹ A pressure regulator for use with the filter-pump is described on p. 238.

to use a funnel provided with a looped suction-tube about 20 cm. long and 4 to 5 mm. internal diameter. The funnel stem is cut short, and the suction-tube fused on, as shown in Fig. 19.

In using either the filter-pump or a suction-tube it is most important that the filter paper should fit the funnel properly, and that no air can leak along the folds of the paper at either side. If air-leakage sets in, the edge of the paper should be firmly pressed into contact with the funnel by means of the stirring-rod. Once suction has been established with a suction-tube, the filter should not be allowed to empty until all the liquid has been filtered.

Paper-pulp Filter.—It is often convenient to filter through paper-pulp, instead of using an ordinary filter paper. A paper-pulp filter is prepared as follows:—Tear a 9-cm. filter paper into small pieces and shake the paper with dilute nitric acid in a small flask until it is completely disintegrated. Place a perforated porcelain disc about 2 cm. in diameter in a 7-cm. funnel, cover the disc with a circle of filter paper, and pour the pulp on the disc, using gentle suction (Fig. 18). Press the pulp down gently with a flat ended glass rod and wash it with warm water until free from acid.



FIG. 19.

SUGGESTED READING

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PART II

VOLUMETRIC ANALYSIS

VOLUMETRIC methods of analysis, although based on a great variety of chemical reactions, present certain common features, and a quantitative determination by volumetric methods usually involves :—

- (1) The preparation of one or more solutions of accurately known concentration ;
- (2) The use of instruments by means of which the volumes of the solutions employed can be quickly and accurately measured ;
- (3) Some means of recognising the completion of the chemical change involved.

Many volumetric methods are of great practical value on account of their simplicity, rapidity, accuracy, and wide applicability. The following example, omitting certain experimental details, illustrates the general features of a simple determination.

Suppose the amount of sodium chloride in a given solution is to be determined. A solution of silver nitrate of known concentration is prepared by dissolving an accurately weighed amount of pure silver nitrate in water and making up the solution to a definite volume. A suitable quantity of the sodium chloride solution is accurately measured into a stoppered bottle, a little nitric acid is added, and the silver nitrate solution is added, in small portions at a time. After each addition of the silver nitrate solution, the mixture is vigorously shaken in order to coagulate the silver chloride and leave the supernatant liquid clear. It is then easy to observe that, when all the chloride has been converted into silver chloride, the addition of another drop of silver nitrate solution produces no further precipitate. This point is called the “end-point” of the reaction. The process involved in the comparison of one solution

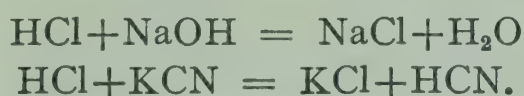
with another by a volumetric method such as this is called "titration."

In this way it is possible to determine accurately the *volume* of silver nitrate solution necessary to precipitate all the chloride. Now this volume of silver nitrate solution contains a definite *weight* of silver nitrate which can readily be calculated since the concentration of the silver nitrate solution is known; and since 169.9 grams of silver nitrate interact with 58.45 grams of sodium chloride, it is easy to calculate the amount of sodium chloride in the solution once the weight of silver nitrate equivalent to it is known.

Classification of Reactions.—The various methods used in volumetric analysis can be classified as follows :—

(1) *Metathetic Reactions* :

(a) Formation of an undissociated compound. Typical reactions are



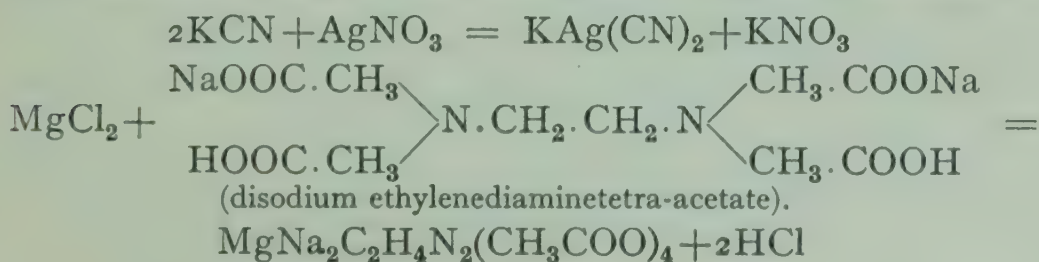
In each case a compound is formed (water and hydrocyanic acid in the cases given) which is practically undissociated in solution. When an acid is used to titrate a base or the salt of a weak acid, the process is called *acidimetry*; the term *alkalimetry* is used for the titration with bases of acids or the salts of weak bases. A further example of this type of reaction is the titration of mercuric ions with chloride ions to form the slightly dissociated mercuric chloride, but this reaction is different in kind from the *neutralisation* reactions used in acidimetry and alkalimetry.

(b) Formation of a precipitate. Typical reactions are :



When silver nitrate is used as reagent the process is known as *argentimetry*.

(c) Formation of a soluble complex. Typical reactions are :



(2) *Electron Transfer Reactions*: These are generally referred to as *oxidation-reduction* reactions, and involve the transfer of electrons to convert ions from one valence state to another. Typical reactions are:



Suitability of Reactions.—Not all reactions are suitable for use as volumetric methods. It is essential that the reaction should be rapid, stoichiometric, free from side reactions or interferences and that it should give a sharp, easily detectable end-point.

Standard Solutions.—Any solution of accurately known concentration is called a *standard* solution. Standard solutions may sometimes be prepared by dissolving an accurately weighed quantity of the substance in water and making the solution up to a definite volume; *e.g.* standard solutions of silver nitrate and sodium carbonate may be prepared in this way. Often, however, the material to be used contains an unknown amount of impurity, or it may be found unsuitable for weighing because it is deliquescent or efflorescent. In such cases, a solution of approximately the required concentration is prepared, and the exact concentration is then found by titration against some suitable substance. For example, a standard solution of sulphuric acid may be prepared by making a solution of approximately the desired concentration on the assumption that the concentrated acid contains 96 per cent. by weight of H_2SO_4 , and then finding the exact concentration by titration against accurately weighed quantities of pure sodium carbonate.

It is desirable that standard solutions should be standardised by the method that will be used in the determinations for which the reagent is employed. It will generally be found that the results obtained when a solution is standardised by different methods do not agree exactly. The reason for this is not solely a statistical one. Small errors may arise from such factors as the different behaviour of various indicators, or the effects of salt hydrolysis, or changes in ionic strength, and so on. For details of these errors a specialist text must be consulted. If the solution is standardised by the method for which it will

subsequently be used, there will be at least a partial compensation of these errors.

One of the great advantages of volumetric work is the ease with which experiments can be repeated. In determinations as well as in standardisations it should be made the rule that titrations are repeated until good agreement between two or more consecutive results is obtained.

Normal Solutions. — For the sake of uniformity and especially for convenience in calculations, it is desirable to prepare standard solutions that contain one gram-equivalent (or a simple fraction of the gram-equivalent) of the reacting substance per litre. A solution that contains one gram-equivalent of the reacting substance per litre of solution is called a *normal* solution.

The gram-equivalent of a substance is the weight of the substance, in grams, that is chemically equivalent to 8 grams of oxygen, or to 1.008 grams of hydrogen.

A normal solution of hydrochloric acid (which is monobasic) therefore contains 36.47 grams (the gram-molecular weight, or molar weight) of HCl per litre; a normal solution of sulphuric acid (which is dibasic) contains 49.04 grams (half the molar weight) of H₂SO₄ per litre; and normal solutions of sodium hydroxide and sodium carbonate contain, respectively, 40.00 grams of NaOH and 53.00 grams of Na₂CO₃ per litre.

Many important volumetric methods are based on oxidation and reduction processes, and a normal solution of an oxidising agent is one that is capable of yielding one gram-equivalent, or 8 grams, of "available" oxygen per litre. Potassium permanganate is an example of an oxidising agent which is used in volumetric analysis for the determination of various oxidisable substances. Titrations with potassium permanganate are carried out in presence of an excess of dilute sulphuric acid, and, as the following hypothetical equation shows, only part of the oxygen of the permanganate is "available" oxygen:



Of the 8 oxygen atoms in 2KMnO₄, only 5 are "available" for the oxidation of the reducing substance present. Since 2KMnO₄ (316.1 grams) yields 5[O], or 80 grams of available oxygen, a normal solution of potassium permanganate, used

as an oxidising agent in the manner indicated, will contain $316.1/10 = 31.61$ grams of the salt per litre.

It is important to realise that, as in the case of potassium permanganate, the chemical equivalence of one and the same substance sometimes varies with the type of interaction in which it plays a part. Potassium tetroxalate, for example, may be used for standardising sodium hydroxide solution (see p. 92), and the gram-equivalent is *one-third of the molar weight*, or 84.7, because the molecule, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, contains three replaceable hydrogen atoms; but if the salt is to be used as a reducing agent for standardising potassium permanganate solution, *one-fourth of the molar weight*, or 63.55 grams, is equivalent to 8 grams of oxygen (or 1 litre of normal permanganate solution) because the oxidation of the molar weight requires 32 grams of oxygen.¹

Normal solutions are found to be too concentrated for many purposes, and more dilute standard solutions, which may be *seminormal*, *decinormal*, etc., are then used instead. When a standard solution is not exactly normal, the concentration is always expressed in terms of a normal solution. Thus, a solution of hydrochloric acid containing 36.76 grams of HCl per litre is $\frac{36.76}{36.47} = 1.008\text{N}$; and a solution of potassium permanganate containing 3.145 grams of KMnO_4 per litre is $\frac{3.145}{31.61} = 0.0995\text{N}$, the symbol "N" being used as a contraction for normal.

Determination of the End-Point in a Titration

Various means are available for determining the end-point in a titration. These may be classified as follows:—

- (1) A permanent precipitate is formed, *e.g.* as in the titration of potassium cyanide with silver nitrate.
- (2) A precipitate just ceases to be formed, *e.g.* as in the titration of silver nitrate with sodium chloride (without potassium chromate).

¹ In the case of a substance which has a different equivalent weight in different reactions, it is advisable, in addition to the normality for the usual reaction, to label its solution also in terms of *molarity*, *i.e.* the number of gram-molecules of the substance per litre of its solution.

- (3) A faint tint is obtained throughout the titrated solution, owing to the addition of a slight excess of a solution which possesses a strong colour ; *e.g.* as in titrations with potassium permanganate.
- (4) A colour change is produced by the addition of a slight excess of the added solution in a substance called an "indicator," which may be mixed with the titrated solution, or used externally. Such indicators include those used in acidimetry and alkalimetry, and substances such as starch, potassium ferricyanide, potassium chromate, diphenylamine, etc.
- (5) A sudden change is produced in the electrical conductivity of the titrated solution, as in acidimetry and alkalimetry, and in certain precipitation analyses.
- (6) A rapid alteration is produced, by a series of small additions of a reagent, in the potential difference between a suitable electrode immersed in the titrated solution and a standard electrode. This method is used in acidimetry and alkalimetry, and in oxidation and reduction reactions.
- (7) The appearance or disappearance of fluorescence in a solution, to which a suitable organic substance has been added, this being occasioned by a very small change in the hydrogen ion concentration of the solution. In ultra-violet light acid-alkali titrations can be carried out in highly coloured or turbid solutions.

The method selected will depend on the type of reaction involved, and on any interfering substances present. For instance, in the case of a solution of acid or alkali which contains coloured impurities, an electrometric method may give a much more satisfactory result than one involving the use of indicators.

It will be noticed that in several of the above methods a slight excess of the added reagent is necessary. In these cases, the end-point of the titration will not correspond exactly with the stoichiometrical or equivalent point as required by the equation for the reaction. The excess can be determined approximately by ascertaining the volume of the titrating liquid required to produce the necessary change of colour in

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the indicator, when this alone is present in a volume of liquid equal to that of the final volume of the titrated solution.

As the matching of the final tint may be uncertain, a more accurate result may be obtained by making a series of titrations using different volumes of the titrated liquid, say in the ratio 1 : 2.5 : 5 (10 ml., 25 ml., and 50 ml.), working to the same final tint in each case. Then if x is the excess required, and V_1 , V_2 , and V_3 are the observed volumes run in from the burette, V_0 being the correct volume required for 10 ml., $5V_0 + x = V_3$; $2.5 V_0 + x = V_2$; $V_0 + x = V_1$. From these equations a mean value for V_0 can be calculated.

THE MEASUREMENT OF VOLUMES OF LIQUIDS

For the measurement of the volume of a liquid, various graduated glass instruments are used, the most important being *pipettes*, *burettes*, *graduated flasks*, and *measuring cylinders*.

Flasks.—Flasks are used in volumetric analysis mainly for the measurement of comparatively large volumes, *i.e.* for volumes of 100 ml. and upwards. A flask is usually graduated to *contain* a definite volume of liquid.

Pipettes.—A pipette is used to *deliver* one specified volume of liquid. Pipettes are made in various sizes, from 1 ml. up to 100 ml. or more. The 10 ml. and 25 ml. are the most generally useful sizes.

Burettes.—A burette is used to deliver, not a fixed volume of a liquid, but any specified volume up to its total capacity. For ordinary work a 50 ml. burette is commonly used.

Measuring Cylinders.—Open-type measuring cylinders are useful for delivering approximate volumes of liquids. For making up solutions of approximately known concentration, cylinders closed at the top with a glass stopper are useful, since mixing can be carried out conveniently in the cylinder.

The Unit of Volume

The fundamental unit used in measuring the volume of a liquid is the **litre**. The litre is defined, not as a cubic decimetre (the original definition) but as the volume occupied by one

kilogram¹ of water at its temperature of maximum density, and subjected to the normal atmospheric pressure. The apparent weight in air of water which occupies one litre at the temperature of maximum density will be less than one kilogram, because of the effect of the buoyancy of air. The apparent weight will be still less when the determination is made at ordinary room temperature, because of the then lower density of water. These factors must be allowed for in determining the volume of a piece of apparatus by weighing the water it contains or delivers. The thousandth part of a litre, *i.e.* a **millilitre**, is not exactly equal to a thousandth part of a cubic decimetre, *i.e.* a **cubic centimetre**, but for all practical purposes the difference is entirely negligible.²

An effort is being made in all countries to replace the cubic centimetre by the millilitre, not because of the minute error involved, but to avoid the haphazard use of the term cubic centimetre for three different meanings, (1) the true cubic centimetre, (2) the true millilitre, (3) the unit of volume as defined by Mohr, which is the volume at 60° F. of that quantity of water which, when weighed in air with brass weights, has an apparent weight of one gram. This unit, denoted "G.W.A." (grams of water in air), is as much as 0.2 per cent. larger than the millilitre, *i.e.* 1000 G.W.A. equals 1002 ml. It is rarely used now. The British Standards Institution now uses the millilitre in all British Standard Specifications. As it is obviously desirable to use a fraction of the universally accepted larger unit, rather than one derived from an entirely different system, the millilitre is used instead of the cubic centimetre throughout the present edition of this book. For a full account, see British Standard 501, 554: 1952.

Measuring instruments as bought may be inaccurate. The experimental determination of the errors in the graduation or

¹ The original kilogram known as the "Kilogramme des Archives" based on the mass of a cubic decimetre of water at 4° C., was superseded in 1889 by an International standard, the "Prototype Kilogram," consisting of a platinum iridium alloy, the mass of which was made as nearly as possible equal to that of the "Kilogramme des Archives." Copies of the prototype kilogram have been distributed to various countries throughout the world.

² The litre, as defined by reference to the standard kilogram, has been found by direct experimental determination to be equal to 1000.028 c.c., *i.e.* 1 ml. is equal to 1.000028 c.c.

the instrument is called *calibration*. If the graduations are altered or adjusted so as to make the instrument accurate, it is said to be *standardised*. Graduated instruments, the accuracy of which has been determined at the National Physical Laboratory,¹ Teddington, may be obtained. Two classes of tests are made at the Laboratory, Class A tests for apparatus to be used for work requiring great accuracy, and Class B tests for apparatus intended for ordinary use. The limits and tolerances allowed for these two grades are given under the descriptions of the various instruments. For a capacity not given in any table, the data corresponding to the next larger capacity must be taken. The instruments are marked with the Laboratory monogram, **NPL**, the class to which they belong, and the year of testing. Measuring instruments of ordinary commercial quality should be standardised or calibrated by the user.

Since the volume of a glass vessel varies with the temperature, it is necessary to select some definite temperature at which the vessel will hold the volume marked upon it. In this country 20° C. has been chosen as the standard temperature, and is marked on the apparatus by the makers. All measurements can then be referred to this standard temperature.

In order to determine the volume delivered by or contained in a piece of apparatus, it is necessary to weigh the water delivered by or contained in it at some particular temperature, preferably near to the standard temperature. It is then necessary to calculate what the volume of the water so weighed would be *in vacuo* at the standard temperature, making use of the known values of the density of water at different temperatures, and applying corrections for the effects of the buoyancy of air and the expansion or contraction of the glass, if this is at a temperature other than 20° C.

By using the tables² opposite these calculations may be avoided. The figures corresponding to the particular temperature and volume concerned indicate the number of grams to be added to the weight in grams of water contained in or

¹ The Laboratory regulations are given in detail in the pamphlet *Tests on Volumetric Glassware*, which may be obtained, free of charge, on application to the Director, The National Physical Laboratory, Teddington, Middlesex.

² Compiled from British Standard 1797 : 1952. By courtesy of the British Standards Institution several British Standards have been drawn upon for the information in the following pages.

delivered by a graduated vessel in order to obtain the numerical value of the volume in millilitres at 20° C.

The corrections given in the table assume that the weighings

t°C.	Nominal capacity of soda-glass vessel in millilitres.								
	5.	10.	20.	25.	50.	100.	250.	500.	1000.
10	0.008	0.016	0.033	0.041	0.081	0.163	0.41	0.81	1.63
11	0.008	0.017	0.034	0.042	0.085	0.169	0.42	0.85	1.69
12	0.009	0.018	0.035	0.044	0.088	0.177	0.44	0.88	1.77
13	0.009	0.019	0.037	0.047	0.093	0.186	0.47	0.93	1.86
14	0.010	0.020	0.039	0.048	0.098	0.196	0.49	0.98	1.96
15	0.010	0.021	0.042	0.052	0.104	0.208	0.52	1.04	2.08
16	0.011	0.022	0.044	0.055	0.110	0.220	0.55	1.10	2.20
17	0.012	0.023	0.047	0.059	0.117	0.234	0.59	1.17	2.34
18	0.012	0.025	0.050	0.062	0.125	0.249	0.62	1.25	2.49
19	0.013	0.027	0.053	0.066	0.133	0.265	0.66	1.33	2.65
20	0.014	0.028	0.056	0.071	0.141	0.282	0.71	1.41	2.82
21	0.015	0.030	0.060	0.075	0.150	0.300	0.75	1.50	3.00
22	0.016	0.032	0.064	0.080	0.160	0.320	0.80	1.60	3.20
23	0.017	0.034	0.068	0.085	0.170	0.340	0.85	1.70	3.40
24	0.018	0.036	0.072	0.090	0.181	0.361	0.90	1.81	3.61
25	0.019	0.038	0.077	0.096	0.192	0.383	0.96	1.92	3.83

t°C.	Nominal capacity of borosilicate glass vessel in millilitres.								
	5.	10.	20.	25.	50.	100.	250.	500.	1000.
10	0.007	0.014	0.029	0.036	0.071	0.143	0.36	0.71	1.43
11	0.008	0.015	0.030	0.038	0.076	0.151	0.38	0.76	1.51
12	0.008	0.016	0.032	0.040	0.081	0.161	0.40	0.81	1.61
13	0.009	0.017	0.034	0.043	0.086	0.172	0.43	0.86	1.72
14	0.009	0.018	0.037	0.046	0.092	0.184	0.46	0.92	1.84
15	0.010	0.020	0.040	0.049	0.099	0.198	0.49	0.99	1.98
16	0.011	0.021	0.042	0.053	0.106	0.212	0.53	1.06	2.12
17	0.011	0.023	0.046	0.057	0.114	0.228	0.57	1.14	2.28
18	0.012	0.025	0.049	0.061	0.123	0.245	0.61	1.23	2.45
19	0.013	0.026	0.053	0.066	0.132	0.263	0.66	1.32	2.63
20	0.014	0.028	0.056	0.071	0.141	0.282	0.71	1.41	2.82
21	0.015	0.030	0.060	0.076	0.151	0.302	0.76	1.51	3.02
22	0.016	0.032	0.065	0.081	0.162	0.324	0.81	1.62	3.24
23	0.017	0.035	0.069	0.086	0.173	0.346	0.86	1.73	3.46
24	0.018	0.037	0.074	0.092	0.185	0.369	0.92	1.85	3.69
25	0.020	0.039	0.079	0.098	0.197	0.393	0.98	1.97	3.93

are made in air at 760 mm. If the barometric height is not exactly 760 mm., an additional correction may be made for variation in air density. This correction is very small, however,

and may be neglected in calibrating apparatus for work of ordinary accuracy. Thus for a litre flask at 20°C ., the correction for a difference in barometric pressure of ± 30 mm. above or below 760 mm. is only ± 0.04 gram, which is only one-fifth of the B.S.S. Class A tolerance (± 0.2 ml.) on a flask of this capacity. The correction for an extreme variation in humidity is even less.

The use of the tables is illustrated by the following examples :—

- (1) 34.91 grams of water at 18°C . were delivered by a soda-glass burette between the 0 and the 35 ml. mark. From the table the total amount to be added in this case to the apparent weight is $0.025 + 0.062$, *i.e.* 0.087. The required volume in mls. is therefore $34.91 + 0.087$, *i.e.* 34.997 at 20°C .
- (2) The tables may also be used to find the amount of water at $t^{\circ}\text{C}$. that must be weighed out to occupy a specified volume at 20°C . *E.g.* the water to be weighed out at 13°C . in the case of a 250 ml. borosilicate flask is $250 - 0.43$, *i.e.* 249.57 grams.
- (3) When a solid is weighed, dissolved, and titrated with a solution the temperature of which is appreciably different from the standard temperature, a slight error will occur. This is because the normality of the solution will change slightly on expansion or contraction of the liquid. This small error may be calculated approximately by means of the tables on p. 55. The difference between the correction for 20° and that for the temperature of the solution must be added to the observed volume used.

Thus in the case of a titration from a soda-glass burette requiring 50 ml. at 11° , the true volume at the standard temperature would be approximately $50 + (0.141 - 0.085)$, *i.e.* 50.06 ml.

This error will not arise when two dilute solutions at the same temperature are being titrated, since each will expand or contract almost exactly to the same extent.

STANDARDISATION OF A FLASK

The flask should be provided with a well-fitting stopper made of glass or plastic material, and should have a long narrow neck (Fig. 20). British Standard 1792 : 1952 lays down mandatory dimensions for the internal diameter of the neck and for the position of the graduation mark relative to the stopper and the place the neck begins to expand at the junction with the bulb. There should be sufficient air space above the mark to allow of liquids being thoroughly mixed by a reasonable number of inversions and shakings of the flask.

The dimensions for the neck are summarised below.¹

Nominal capacity.	Internal diameter of neck.			Minimum distance of graduation mark from top of neck.	Minimum distance of graduation mark above point at which neck begins to expand into bulb.		
	Minimum.	Maximum.			Classes A and B.	Class A.	Class B.
		Classes A and B.	Class A.				
ml.	mm.	mm.	mm.	mm.	mm.	mm.	
5	6	7	8	25	5	5	
10	6	7	8	25	5	5	
25	7	8	10	30	5	5	
50	8	10	12	30	10	10	
100	10	12	14	40	10	10	
250	12	14	16	60	20	10	
500	14	17	19	60	20	10	
1000	16	20	22	70	20	10	
2000	22	26	28	80	20	10	

In addition to the graduation mark for "content," Class B flasks may also be so graduated that they will deliver a measured volume of liquid. Flasks intended for "delivery" are emptied by gradually inclining them, until, when the continuous stream of water has ceased, the neck is nearly vertical. In this position the flasks are allowed to drain for half a minute, during which time the edge of the neck is kept in contact with the inside of the receiving vessel, and at the end of the draining time any drop of water adhering to the edge of the neck is removed against the inside of the receiving vessel. Flasks graduated for "delivery" as well as "content" must bear the letter D above the upper mark and the letter C below the lower mark, and these marks must not be less than 1 mm. apart.

¹ The table is taken from British Standard 1792 : 1952.

Standardisation.—Clean the flask thoroughly,¹ and set it aside inverted until it is dry, hastening the process by drawing through it a slow current of air by means of a water-pump. The process is much more rapid if the vessel is first rinsed with pure acetone. Weigh the flask on a suitable balance. (The weighing should be accurate to within 0.01 gram for a 100 ml. flask and to within 0.05 gram for a litre flask. A special balance, capable of supporting the heavy load, is required for flasks larger than 100 ml.) Fill the flask to the graduation mark with water preferably at a temperature of from 19° to 21°.

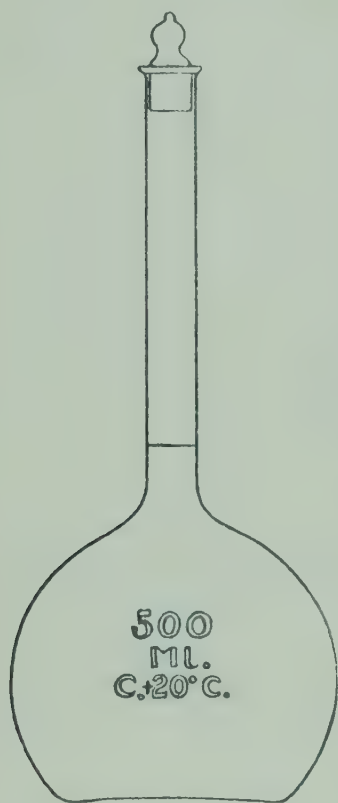


FIG. 20.

Examination of the surface of the water in the neck of the flask will show that it is not flat but curved, and the level of the water must be adjusted so that the *lowest* point of the curved surface (the meniscus) coincides exactly with the graduation mark.

Error from parallax is avoided when the front and back of the graduation mark are seen as a single line. The meniscus will be clearly visible if the flask is placed before a window at some distance away from it, but in artificial light

¹ It is essential that volumetric apparatus be thoroughly clean before use. Deposits on the glass must be dissolved off by suitable reagents. The presence of grease will be shown by the formation of drops on the surface of the glass after liquid is run out. In this latter case, the vessel must be treated by one of the following methods until the surface remains uniformly wet after emptying.

- (1) Grease may be removed by prolonged treatment with chromic acid solution, a mixture of saturated potassium dichromate solution and concentrated sulphuric acid in the ratio of approximately 5 : 4 by volume being used. This is slow but efficient. It is best to fill the vessel and set it aside overnight. A pipette may be kept full by filling almost to the top, inserting a length of rubber tubing fitted with a clip between the mouth and the pipette.
- (2) A much quicker method consists in washing out the vessel with a few millilitres of benzene. After draining this off, a few millilitres of concentrated sulphuric acid are introduced, and this is similarly brought into contact with the whole surface, and then poured out. Subsequent washing with distilled water leaves a perfectly clean surface, unless the vessel has been exceptionally greasy, in which case the process must be repeated.

it should be viewed when held two or three feet away from a white surface. The adjustment of the water level is made by first adding water to a few millimetres below the mark, but without wetting the sides of the neck above the water surface, and then adding water with a glass tube drawn out to a capillary.

Weigh the flask filled with water, and from the weight of the water, calculate the volume.

Example.—The following figures were obtained with a 500 ml. soda-glass flask :—

Flask + water	=	565.85	grams
Tare of flask	=	65.20	„
Weight of water	=	500.65	„

The temperature of the water was found to be 14° . From the table on p. 55, it is seen that the weight to be added to the weight of water at 14° in the case of a 500 ml. vessel is 0.98 gram. The flask therefore would have contained 501.63 ml. at 20° .

The flask may be used with application of the necessary correction, but it is more convenient to make a new graduation at the correct place. The position of this mark is found as follows :—Calculate the weight of water that will fill the flask to the correct graduation mark (in the above example, $500 - 0.98 = 499.02$ grams). Place the calculated weight together with the tare of the flask on the balance-pan and adjust the amount of water in the flask until the total weight of the flask and water is found to be correct.

Etching a line on Glass.—A new line should then be etched on the glass at the correct position by means of hydrofluoric acid in the following manner :—Gum on two strips of paper completely round the tube, leaving only a narrow space between them where the line is to be etched (Fig. 21).

Warm cautiously above a flame, and rub with a piece of paraffin wax until the paper is saturated with the melted wax. When it has solidified, remove the wax from the line between

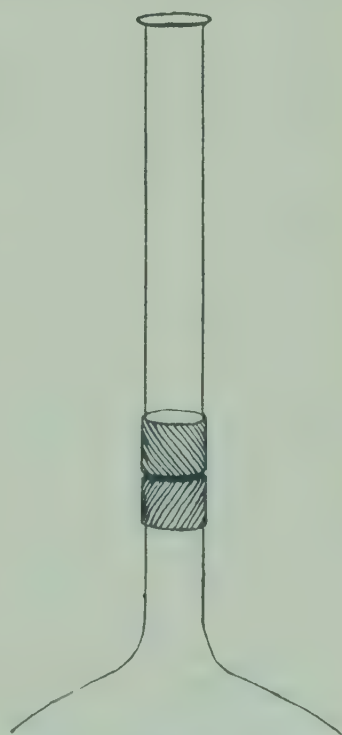


FIG. 21.

the two papers by means of a metal point. Fix a narrow strip of filter paper round this line, and wet the paper with hydrofluoric acid solution. (**Caution.**—Care must be taken that the hydrofluoric acid does not come into contact with the skin, since it causes a particularly painful sore.)

After about ten minutes, wash off the hydrofluoric acid and remove a small portion of the paper and wax to ascertain if the glass is sufficiently etched. If the etching is insufficient, re-wax and repeat the process, but allow more time for the etching action.

The tolerances allowed on graduated flasks ¹ are :—

Capacity ml. Tolerance \pm ml. for content—	10	25	50	100	250	500	1000	2000
Class A . . .	0.02	0.03	0.04	0.06	0.1	0.15	0.2	0.4
Class B . . .	0.03	0.04	0.06	0.1	0.2	0.3	0.4	0.6

USE AND STANDARDISATION OF A PIPETTE

The pipette should first be examined to make sure that it is capable of being used as an instrument of precision. The narrow tubes should not be above 4 mm. internal diameter for a 10 ml. pipette, 5 mm. for a 25 ml. pipette, 6.5 mm. for a 50 ml. pipette, and 7 mm. for a 100 ml. pipette. The graduation mark ² must be at least 6 cm. from the top of the suction tube of pipettes of capacity of 5 ml. or less, and at least 8 cm. from the top of the suction tube of pipettes of capacity greater than 5 ml. The suction tube of the pipette must be cylindrical for at least 1 cm. below the graduation mark on pipettes of capacity 5 ml. or less, and for at least 2 cm. below the graduation mark on pipettes of capacity greater than 5 ml.

A pipette will not deliver constant amounts if it discharges too quickly. The limits for the time of outflow for both Class A and Class B pipettes are shown in the following table ² :—

Capacity ml.	1	2	5	10	30	50	100
Minimum delivery time in seconds Classes A and B	5	7	10	15	20	25	30
Maximum delivery time in seconds Classes A and B	10	15	20	25	35	40	50

¹ British Standard 1792 : 1952.

² British Standard 1583 : 1950.

If the time of outflow is too short, this may be corrected by carefully heating the jet and drawing it out to a gradual taper. A sudden constriction at the jet is not permissible in Class A or B pipettes. This treatment will, of course, alter the volume of liquid delivered by the pipette. If the time of outflow is too long, the end of the jet should be ground on a fine carborundum stone, lubricated with a solution of camphor in turpentine.

A pipette will not deliver a definite volume unless it is used in a specified manner, and the following instructions should be carefully followed.

See that the pipette is absolutely clean (see p. 58), and dry, or rinsed thrice with the liquid, and fill it by applying gentle suction with the mouth until the liquid is 3 to 4 cm. above the mark. Rapidly place the forefinger¹ over the top of the pipette and wipe the outside. Carefully allow a little air to enter past the finger until the bottom of the meniscus is in line with the mark on the pipette, which must be held vertically, and so that the mark is at the same level as the eye. The tip of the pipette should touch a clean glass surface during this process, so as to leave no adhering drop and to prevent the entry of an air bubble at the jet. Keeping the pipette as steady as possible, bring the receiving vessel under the tip of the pipette, remove the finger, and allow the contents to run out, while the tip is held in contact with the glass, which should be slightly inclined to the pipette.

After the continuous discharge has finished, the pipette must be allowed to drain for fifteen seconds with its tip still in contact with the glass. The receiving vessel is then removed, leaving in the jet of the pipette the liquid that is still there.

Standardisation.—Find the weight of an empty weighing-bottle or a small flask, which need not be dried inside. Fill



FIG. 22 —
A Pipette.

¹ Unless the tip of the forefinger that is placed on the upper end of a pipette is smooth and *slightly* moist, it may be found impossible to manipulate the instrument with ease and certainty. If the finger-tip is rough, rub it with pumice; and, immediately before using a pipette, moisten the finger-tip with the lips or tongue and rub the finger and thumb together for a moment.

the pipette to the mark with distilled water, run the contents into the weighing-bottle, and reweigh. Find the temperature of the water and, with the help of the tables on p. 55, calculate the volume of the observed weight of water. If the error is greater than the permissible error (see below), the pipette must be corrected in the following manner.

A rough estimate as to how far to place the new mark from the old graduation may be obtained by noting how far the water sinks in the narrow tube when one drop is run out of the pipette. One drop of water weighs, roughly, about 0.05 gram. Gum a strip of paper along the pipette and make a mark where it is thought the graduation should be.

Weigh the amount delivered by the pipette with this new graduation, and calculate the volume to which this corresponds. If this is not quite correct, it will serve as a guide to the exact position. When it is certain (by a repetition of the weighing) that a mark on the paper is the correct position for the graduation, a line should be etched on the glass at this place (see p. 59). Before removing the paper with the graduation mark, wash off the etching solution and examine a small portion of the line to be sure that it is properly etched.

British Standard 1583:1950 requires that, for the two classes of pipettes, the following tolerances must not be exceeded :—

Capacity ml.	.	2	5	10	20	25	30	50	100
Tolerance \pm ml.	.								
Class A	.	0.01	0.02	0.02	0.03	0.03	0.03	0.04	0.06
Class B	.	0.02	0.03	0.04	0.05	0.06	0.06	0.08	0.12

Standardised pipettes are now usually marked thus :—

50 ml.
D. 20° C.
(30+15) sec.

D. denotes delivery (and not content), thirty seconds is the time of outflow, and fifteen seconds the additional time to be allowed for drainage.

Graduated Pipettes.—Some pipettes, instead of being marked to deliver one specified volume of liquid, have a series of graduations like a burette, and are very useful for rapidly measuring out odd amounts of liquid. They cannot, however, be used with the same precision as the ordinary type of pipette.

USE OF A BURETTE

A burette is a measuring instrument of lower precision than a pipette or graduated flask, and great care is necessary to secure the best results. Precision in carrying out titrations may be improved by slightly greasing the tip by drawing the fingers over it, or by dipping the warmed burette-tip into melted wax, and shaking off any excess. With a fine jet, drops as small as 0.02 ml. may then be obtained.

A burette is usually graduated in tenths of a millilitre. It is fitted at the lower end with a glass tap, so that the flow of liquid may be regulated and stopped as desired (Fig. 23). In order that the measurements with a burette may be accurate, attention must be paid to the following points :—

- (1) The burette must be clean (see p. 58).
- (2) The tap must be lubricated with a mere trace of a suitable lubricant. (Vaseline, or a mixture made by melting one part of *black* rubber with six parts of vaseline will be found satisfactory.) The tap must not leak.
- (3) The burette must be clamped *vertically*, and at a convenient height above the bench. As a rule, it is best to adjust the burette so that the tip of the jet is about half an inch above the top of the receiving vessel.
- (4) The rate of discharge is a very important consideration in the use of a burette, and is dealt with more fully on p. 68. The time taken in delivering the liquid from a 50 ml. burette should be about 150 seconds. In a good burette the jet is of such a size that the proper rate of delivery cannot be exceeded.
- (5) The level of the liquid in a burette is read by noting the graduation opposite the lower boundary of the dark portion of the meniscus (except with opaque solutions as explained on p. 116), and an accurate reading



FIG. 23.

requires (a) suitable illumination of the meniscus, (b) avoidance of parallax error. A simple method of illuminating the meniscus is to hold a white card behind the burette, as shown at M in Fig. 24. The eye must be at the same level as the meniscus; it is evident that readings from positions A or B will be incorrect.

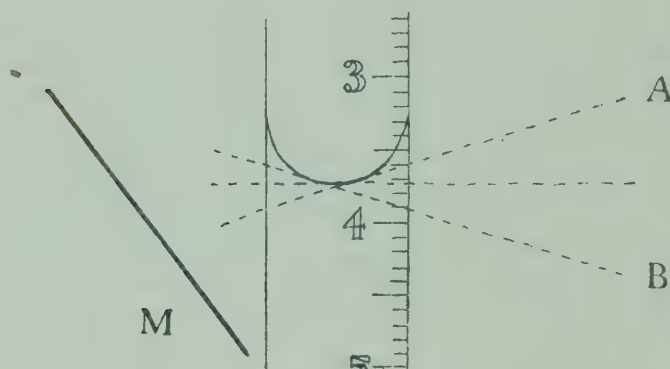


FIG. 24.

Various devices for giving suitable illumination of the meniscus and avoiding parallax error have been designed, of which the following are examples :—

- (1) A device designed by F. C. Guthrie makes it possible to read to 0.01 ml. a burette which is marked with fine lines. It consists of two tubes of brass or aluminium (preferably) of about 0.5 mm. wall, one of which is approximately 7 cm. in length and about 3 cm. in external diameter, and slides loosely inside the other, which is 3 cm. in length and has an internal diameter about 1 mm. greater than the external diameter of the longer tube. From one end of each tube six cuts of 2 cm. in length are made with shears parallel to the axis of the tubes. In each tube two of these cuts are made in the plane of the diameter and the other four about 7 mm. on each side of this plane. The portions of the wall between the cuts are bent at right angles to the axis of the tubes and cut short so that they project about 1 cm. from the walls of the tubes (see Fig. 24a). All corners and rough edges are then filed. The tubes are attached to the burette as shown in Fig. 24a; the slots formed at the end of each tube after bending as described above should be wide

enough to accommodate the burette loosely. The tubes are drawn together with light springs or strong elastic bands one on each side of the device and attached to small hooks soldered to the brass tubes (see Fig. 24*a*). The parts of the walls bent at right angles to the tubes grip the burette tightly enough to prevent the device from falling but allow it to slide freely up and down the burette. A lens of between 5 and 6 cm. focal length is mounted near the outer

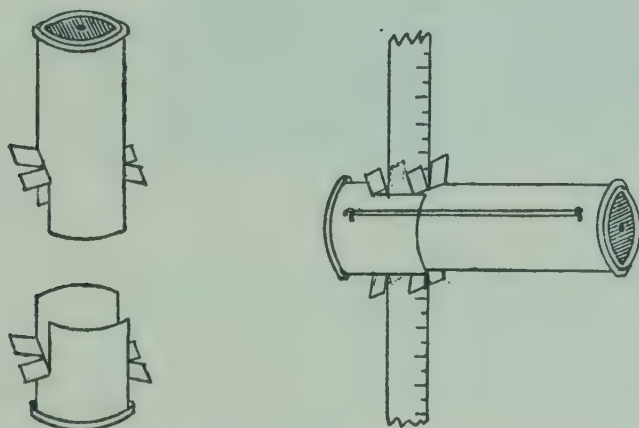


FIG. 24*a*.

end of the longer tube so that it is focussed onto the burette graduations. A light metal or cardboard diaphragm with a central hole of 1.5 mm. diameter is fitted over the end of the longer tube and blackened. A disc of ground glass or tracing paper is fitted over the end of the wider tube by means of a metal flange. This disc gives a diffused illumination which shows up the lower dark edge of the meniscus clearly. The small aperture at the other end not only increases the depth of focus making the meniscus and graduations both clearly defined but it also reduces the parallax error to a negligible quantity. A metal pointer is attached to the inside of the narrower tube along the horizontal radius, extending just short of the axis of the tube so that the graduations on the burette are not obscured. The pointer is placed so that if prolonged it would touch the front surface of the burette. Before the level of the liquid in the burette is read the device is moved up or down until the pointer is level with the liquid meniscus.

- (2) A satisfactory device, which gives good meniscus illumination and eliminates parallax error, is shown in Fig. 25.¹ A piece of white celluloid, measuring about 7 cm. by 4 cm., has two-thirds of its area

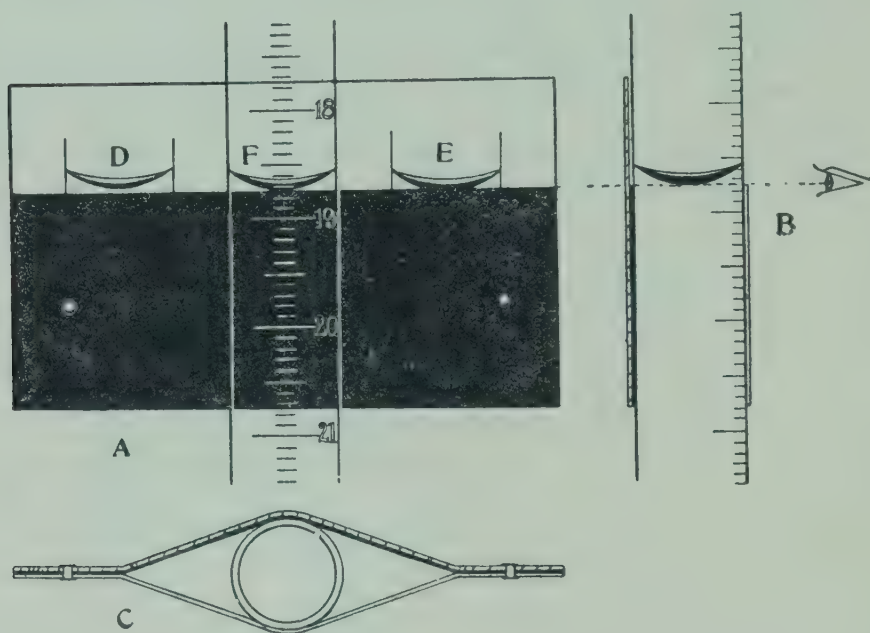


FIG. 25.

blackened, as shown in diagram A ; exactly covering the black area and fixed to it by means of two eyelets is a strip of transparent celluloid. The device is slipped over the burette (as shown in diagram C) and will remain in any desired position. A burette reading is made as follows :—

The device is placed on the burette so that the upper margin of the black area is just below the meniscus. (The meniscus then appears as a black crescent with a very sharp lower outline.) The eye is brought into such a position that the upper edge of the transparent celluloid (in front of the burette) and the upper margin of the black area (behind the burette) are seen as one coincident line, and the device is gradually raised until this line forms a tangent to the black crescent of the meniscus. This is shown in diagram B and also at F. The slightest movement of the eye throws the front and back margins of the device out of alignment, while the

¹ This device may be obtained from Mr A. H. Baird, Lothian Street, Edinburgh.

slightest movement of the device itself causes the meniscus to appear above or below the coincident margins, as shown at D and E. After the device has been adjusted in this manner, the burette reading is obtained, without further reference to the meniscus, by noting the position on the burette of the upper margin of the transparent celluloid. It is possible to read to the nearest 0.01 ml., especially with the aid of a pocket lens.

- (3) Another device is found in the Schellbach burette (Fig. 26) which has a broad, white band along the back and a narrow (usually blue) band in the middle of the white one. The error from parallax is lessened, but is not completely eliminated by this device.



FIG. 26.

When a burette is washed out, the open end should be closed with a cork—not with the finger, because this makes the glass greasy; or the burette may be washed by running in some water and tilting the tube up and down. The tap must not be opened while the burette is inverted, or grease may be introduced from the tap. After a burette has been washed it should be drained as completely as possible, and, before it is filled with a solution, it must be rinsed thrice with a little of the solution in order to remove the water still adhering to the wall and the jet. The solution should be poured into the burette through a small, dry funnel. The funnel must be removed from the burette and the air expelled from the jet before the initial reading is taken.

In titration it is often possible to judge the end-point with a precision of about 0.01 ml. To enable this to be done and to avoid overstepping the end-point, the solution in the burette must be cautiously added in fractions of a drop at a time, when near the end-point. Fractional drops may be removed from the jet of the burette with a stirring-rod, or by bringing the side of the receiving vessel into contact with the jet.

Calibration of a Burette

A burette that is to be used for accurate work must be tested or calibrated, unless it is a verified instrument. The calibration

of a burette demands very careful manipulation on the part of the operator, who must have had previous experience in handling such instruments and must know how to use them properly.

When liquid is run out from a burette a film of liquid is left on the walls and subsequent drainage from this film causes a rise in the level of the liquid surface after the stopcock has been closed. When the liquid is run out quickly a thicker film is left behind than when the burette is emptied slowly and more subsequent drainage occurs. With burettes giving a rapid rate of outflow when the stopcock is fully open, variations in the rate of outflow during use cause appreciable differences in the volume of liquid delivered, and variations in the time which elapses before the reading is taken are accompanied by differences in the observed reading. Such burettes are liable to give inconsistent results because of unavoidable variations in procedure during use. It is possible, however, without making the rate of outflow unduly tedious, so to reduce these variations, by employing a fine jet which prevents rapid outflow, that adequately consistent results can be obtained even with considerable variations in procedure. The times of outflow specified by the British Standards Institution have been so chosen as to achieve this end. They are ¹ :—

Graduated length in centimetres	25	30	35	40	45	50	55	60	65	70
Minimum time of outflow in seconds :										
Class A	50	60	70	80	90	100	110	120	130	140
Class B	35	40	50	55	60	70	75	80	90	95
Maximum time of outflow in seconds :										
Classes A and B	90	105	120	135	150	165	180	195	210	225

The time of outflow is taken with the tap fully open, and the jet *not* in contact with the inside of the receiving vessel.

If the time of outflow does not fall between these limits the jet of the burette can be adjusted by careful treatment. If the delivery is too slow the tip of the burette should be ground on a fine carborundum stone lubricated with a solution of camphor in turpentine. If the delivery is too fast, the jet should be heated and drawn out to a gradual taper. After the surplus glass has been cut off the jet will probably be too

¹ British Standard 846 : 1952.

small and it must then be ground as above until of the required size.

When high precision is required it should be noted that after running out, say, 25 ml. of liquid from a 50-ml. burette with the tap fully open, though no drainage is observed in the first two or three minutes, 0.03 to 0.04 ml. will drain down in fifteen minutes in the case of liquids whose viscosity is not very different from that of water.

Procedure.—Clean the burette very carefully. Lubricate the tap and make sure that it does not leak. Clamp the burette *vertically* at a convenient height above the bench. Fill the burette with distilled water, the temperature of which is the same as that of the room. Record this temperature. Expel air from the jet of the burette. Observing the meniscus with one of the devices described above, carefully adjust the level of the water to the zero graduation of the burette. Remove any drop adhering to the jet by bringing the jet into contact with the side of a beaker.

Water is then run out, with the tap *fully* opened, into a flask which has been weighed to the nearest centigram, until the meniscus of the water is within 1 cm. of the point under test. The speed is then slackened to enable the meniscus to be brought exactly on to the mark. No period of draining should be allowed. Remove any drop adhering to the jet by bringing the inside of the receiving flask into contact with the jet. This procedure is carried out for each of the marks to be tested, say 5, 10, 15, 20, etc. The zero mark is always taken as the starting point, as a very small drainage might take place between readings and impair the accuracy of the intermediate determinations. Repeat the whole process and tabulate the results in four columns: (1) Burette reading, (2) Mean of observed weights of water delivered, (3) True volume at 20° calculated from the data on p. 55, (4) Correction at each mark.

Care must be taken to avoid mistakes in the sign (plus or minus) of the corrections. A plus correction must be added to, and a minus correction must be subtracted from the corresponding burette reading in order to obtain the true volume. By plotting the corrections against the corresponding burette readings, a curve of corrections is obtained. Since the error in reading a burette is about 0.01 ml., the corrections themselves may involve an equal error, and a "smoothed"

curve may therefore be drawn through the points. The correction at any burette reading may be obtained at once from the curve.

It is advisable to reject a burette if there are serious errors, and particularly if there are marked irregularities in it.

The tolerances allowed on burettes ¹ are :—

Total capacity ml.	2	5	10	25	50	100
Maximum error allowed at any point tested, and also maximum difference allowed between the errors at any two points tested						
Class A \pm ml.	0.01	0.02	0.02	0.03	0.06	0.1
Class B \pm ml.	0.02	0.03	0.04	0.06	0.1	0.2

For example, in the case of a 50 ml. burette Class A, an error of $+0.04$ ml. at one point must not be accompanied by an error of -0.04 ml. at another point.

For accurate work it is advisable to calibrate a burette at every millilitre mark, as experience shows that considerable variations are liable to occur with even these small differences of volume.

Weight Burettes

It is obvious (from the foregoing paragraphs and from the statistical treatment given on p. 32) that the precision attainable with a 50 ml. burette is not likely to be better than 1 part per 1000. For specially accurate volumetric work it is necessary to use some other instrument than the normal volume burette. The best of the devices proposed is the weight burette (Fig. 27). The burette is roughly graduated so that the amount of liquid run out may be estimated. It is weighed before and after the titration, and the amount of reagent added is calculated from the difference in weight. The concentration of the reagent is expressed in terms of gram-equivalents per 1000 grams of solution.

It is essential that the other steps of the procedure can be carried out with a precision comparable to that attainable with the weight burette. One of the major difficulties is control of addition of reagent at the end-point, but this may be dealt with by adding a small excess of titrant and back-titrating it with a very dilute solution contained in an ordinary burette.

¹ British Standard 846 : 1952.

The main advantages of the weight burette are the precision attainable, and the elimination of errors from drainage, change in temperature, etc.

GENERAL NOTES ON THE PREPARATION OF STANDARD SOLUTIONS

For obvious reasons it is desirable that a standard solution should not alter in concentration on keeping; volatile or unstable substances are therefore to be avoided if possible.

Solutions more concentrated than *normal* are rarely required in analytical work. More dilute solutions may be prepared with accuracy from a standard N solution by using a *standardised* pipette and flask.

As a general rule, the solution or solid (finely powdered before weighing) from which the standard solution is to be prepared is washed into the standard flask through a funnel with a wide stem. The flask must of course be clean, but it is unnecessary to dry it. Standard flasks should not be heated. If it is necessary to apply heat in the preparation of the solution, this operation should be performed in a beaker, and the solution then cooled before pouring it into the flask. If the solution is prepared in a beaker or other vessel, the volume of liquid must be such that ample wash-water may subsequently be used without exceeding the volume of the standard flask.

Before making up to the mark the contents of the flask must be sufficiently mixed, to ensure that there is no considerable difference in concentration between the top and bottom layers.

To accomplish this the contents of the flask are mixed by rotation when the level is a little below the neck. If this is not done an error is introduced by the change of volume that occurs when mixing takes place.

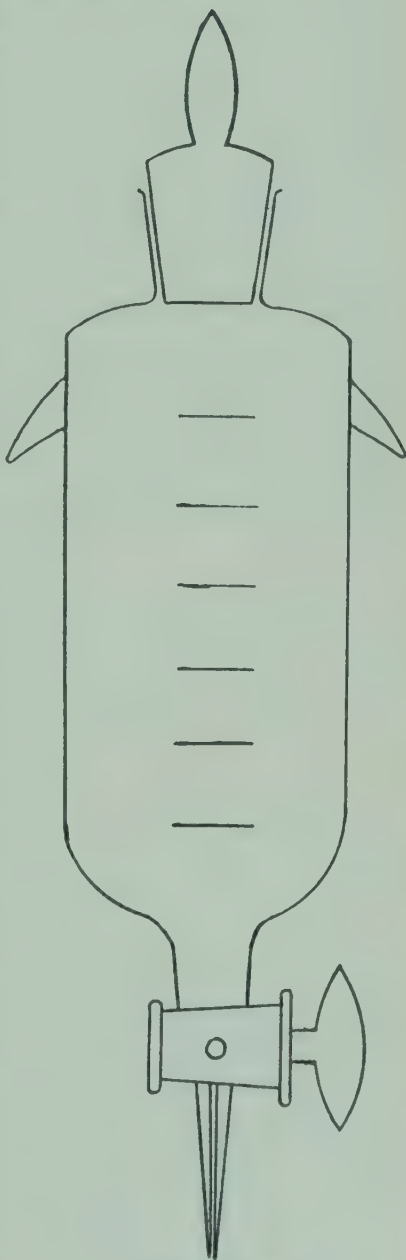


FIG. 27.

The solution should be at or near 20° before it is made up to the graduation mark.¹ Attention to this is specially necessary if the process of dissolution or dilution is accompanied by a considerable heat evolution, *e.g.* with sulphuric acid or sodium hydroxide. In that case it is advisable to dilute almost to the full amount and cool by running tap-water over the flask. The final addition of water to bring the level up to the graduation mark is most easily made from a pipette with a fine jet.

Before any of the liquid is poured out of the flask, the stopper should be firmly inserted and the contents thoroughly mixed by inverting the flask at least ten times and shaking each time. This must on no account be neglected, otherwise serious errors may be introduced.

The solution is best stored in a stoppered bottle. The bottle must be rinsed out two or three times with small quantities of the solution, the portions used for rinsing being rejected. The bottle should be clearly labelled with the name of the solution, the exact concentration, and the date of standardisation. If there is more than one common method for the

Hydrochloric Acid 1.017N (by borax) 31/12/54
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standardisation of the solution, the label should indicate which method was adopted.

When a bottle of standard solution has been set aside for some time, drops of liquid will be found to have condensed on the upper part of the bottle. As these drops differ in concentration from the main portion of the solution it is always advisable to shake the bottle before use. If any sediment is present this should be allowed to settle after shaking. The neck of the bottle should be dried with a lintless cloth after solution has been poured out.

¹ The error introduced is approximately 1 part in 1000 when the temperature is 5° higher, and the solution is being made with a weighed amount of substance.

Preparation of a Standard Solution of a desired Concentration

The usual practice in the preparation of a standard solution is to make the solution of approximately the required concentration, then to determine the exact value, and use this value as a "factor" in the calculations. It is sometimes necessary, however, to prepare a solution which is, for example, *exactly* normal, or decinormal, and the following is an illustration of a method that may be used.

Preparation of an exactly Normal Solution.—In preparing the solution it is better to make it somewhat too concentrated at first rather than too dilute, as it is an easier matter to alter the concentration by addition of water than by addition of weighed quantities of the solute.

Example.—A solution of sodium carbonate was found by titration to be 1.045N. It is clear that 1000 ml. of the solution contain 1.045 equivalents, and that it could be made exactly normal by increasing the volume to 1045 ml. If 45 ml. of water were added to 1 litre of the solution, there would then be 1.045 equivalents in *about* 1045 ml.¹

The approximate volume of the solution is determined by means of a measuring cylinder. Suppose, for example, the volume of the sodium carbonate solution was found to be 440 ml. The amount of water to be added is then

$$\frac{440}{1000} \times 45 = 19.8 \text{ ml.}$$

The 19.8 ml. of water is run out from a burette into the solution in the measuring cylinder. (Take care to add too little rather than too much water.) The solution is poured back into the bottle, shaken, and again titrated with standard acid. If it is still too concentrated, again add the calculated amount of water and again titrate. After the second adjustment the solution should be of the required concentration; if not, continue the process. After adding any water, always return the solution to the bottle and shake it before titrating it with the acid.

¹ Addition of 45 ml. of water will not give exactly 1045 ml. The volume obtained when a solution is diluted with water is slightly less than the sum of the volumes taken, but the difference is so small that it may be neglected except with concentrated solutions.

Use of a Standard Solution of Arbitrary Strength

In commercial analyses, where many similar determinations of the same constituent are to be made, standard solutions are often prepared of such a strength that the number of millilitres required in a titration indicates without further calculation the required proportion of the constituent present.

CALCULATIONS IN VOLUMETRIC ANALYSIS

When a solution whose strength has to be determined has been titrated against a known standard solution, the weight of substance in the former, or the weight per litre as may be desired, can then be calculated, by means of the chemical equation for the reaction employed, from the known weight of reagent in the volume of the standard required. This method has been adopted in this book.

It is usual in practice, however, to mark standard solutions with their normality only, and in this case a more rapid calculation may often be made by means of the equation

$$N_1V_1 = N_2V_2,$$

where N_1 and V_1 are the normality and volume of one solution taken, and N_2 and V_2 the normality and equivalent volume of the other. From the normality of the unknown solution thus found, the grams per litre of the required constituent can then be calculated from its equivalent weight for the reaction employed.

The relation $N_1V_1 = N_2V_2$ is also useful in making up standard solutions from more concentrated ones: *e.g.* if 250 ml. of a 0.015N solution is to be prepared from a 0.95N solution, the volume of the latter to be made up in a graduated flask will be $\frac{250 \times 0.015}{0.95}$ ml.

When a known weight, W grams, of a substance is used in an indefinite volume, V ml., of liquid, the normality of this solution, N , will be $\frac{1000W}{EV}$, and NV will be $\frac{1000W}{E}$, E being the equivalent weight for the reaction of the substance whose weight only is known.

Acidimetry and Alkalimetry

THE determination of the concentration of acids by means of standard alkali solutions is known as acidimetry, and the reverse process as alkalimetry. The choice of acids and alkalis for standard solutions is partly a matter of convenience, but for certain purposes the choice is restricted, *e.g.* a standard sodium carbonate solution cannot be used instead of a standard sodium hydroxide solution for the determination of a weak acid such as acetic acid.

Standard Acids.—The only acids in common use are hydrochloric and sulphuric acids. The preparation of normal solutions of each, with various methods of standardisation, will be found below; more dilute standard solutions are best prepared by dilution of the normal solution.

Standard Alkalis.—Sodium hydroxide, sodium carbonate, and barium hydroxide are all used for standard solutions, and each has advantages over the others for special purposes. The selection of an indicator is of special importance in connection with standard alkalis; and it is advisable that in standardising and in subsequently using a standard alkali, the same indicator should be used.

NOTES ON THE USE OF INDICATORS

The indicators used in acidimetry and alkalimetry are sometimes said to show when a solution is neutral, but this is only approximately true.

A neutral solution is one in which the concentrations of the hydrogen ion H^+ and the hydroxyl ion OH^- are equal, and are each approximately 1×10^{-7} gram ions per litre (10^{-7} N), as in ideally pure water. If the concentration of the hydrogen ion is greater than that of the hydroxyl ion, the solution is acid; if it is less than that of the hydroxyl ion, the solution is alkaline. In pure water and in all dilute aqueous solutions, whether acid, neutral, or alkaline, the product of the concentrations of hydrogen ion and hydroxyl ion is constant and is approximately 1×10^{-14} . If, for example, the

hydrogen ion concentration is 10^{-5} N, then the hydroxyl ion concentration is 10^{-9} N, and the solution is acid; if the hydrogen ion concentration is 10^{-8} N, the hydroxyl ion concentration is 10^{-6} N, and the solution is alkaline.

Those acids and alkalis which are almost completely ionised in dilute solution are described as "strong." Acids and alkalis which are largely undissociated in dilute solution are described as "weak." With a few exceptions salts are almost completely ionised in solution. When equivalent amounts of acid and alkali are mixed, salt formation will be incomplete if the acid, or alkali, or both are weak. This arises from the complete dissociation of the salt in solution and the weak dissociation of the water and the acid or base (or both). Suppose an equivalent amount of a strong base is added to a weak acid, and suppose that momentarily the reaction is complete and that an equivalent amount of the salt is formed. In solution the salt ionises, and the anion will combine with the hydrogen ions arising from dissociation of the water and will form undissociated acid. More water will dissociate to maintain the equilibrium constant, and more undissociated acid will form. The process will continue until an equilibrium is attained. Meanwhile there has been a steady accumulation of hydroxyl ions in the solution from the dissociation of water, and the solution will be strongly alkaline. By similar reasoning it is obvious that when equivalent amounts of a strong acid and a weak base are mixed, the solution will be acid. The phenomenon is referred to as salt hydrolysis.

It is customary to speak of all solutions, whether acid or alkaline, in terms of their hydrogen ion concentration, and in order to avoid long decimals or negative indices, and to enable the whole range of acids and alkalis to be readily graphed, a logarithmic device is used. As the logarithm of the actual hydrogen ion concentration would usually be negative, the logarithm of the reciprocal is taken, this being called the pH of the solution. If cH is the hydrogen ion concentration in grams per litre,

$$pH = \log \left(\frac{1}{cH} \right).$$

For example, the hydrogen ion concentration of decinormal hydrochloric acid is about 0.093 gram per litre. $1/cH = 10.7$,

and $\log 10 \cdot 7 = 1 \cdot 03$. The pH of this acid solution is therefore $1 \cdot 03$. Similarly, the pH of decinormal sodium hydroxide solution, which has a hydrogen ion concentration of about $1 \cdot 175 \times 10^{-13}$ gram per litre, is $12 \cdot 93$. The pH of pure water is approximately 7.

The use of pH , though so convenient, tends to be misleading at first, and the following points should be noticed. Acid solutions have a pH less than 7, and alkaline solutions a pH greater than 7, the pH value increasing as the hydrogen ion concentration falls. A unit change in pH means a tenfold change in hydrogen ion concentration. The mean hydrogen

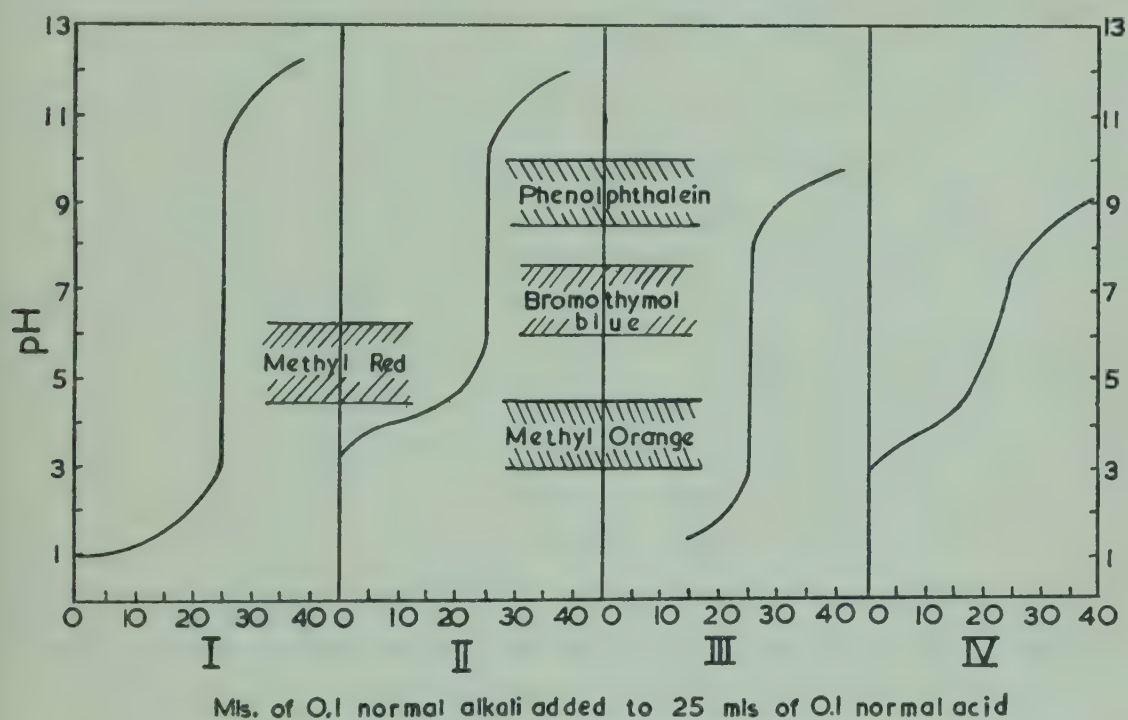


FIG. 28.

ion concentration between pH 2 and pH 3 is not represented by pH 2.5, but by pH 2.3.

The pH of a solution can be determined most accurately by an electrometric method (see p. 213). If the series of pH readings obtained when a strong (*i.e.* highly ionised) alkali is gradually added to a strong acid is plotted, a curve of the type shown in Fig. 28 I is obtained, in which a large change in pH produced by a small addition of alkali at a certain point is seen to occur.¹

The curve becomes almost parallel with the pH axis for some distance, and then bends away again. This region of abrupt change shows the existence of a stoichiometric point.

¹ If the titration is carried out by the addition of acid to alkali, the shape of the curves in Fig. 28 will be inverted.

When acid and alkali are both strong, the portion of the curve parallel to the pH axis extends over a considerable range of pH ; but if either is weak, the parallel portion is shorter. This is illustrated by curve II (Fig. 28), representing the titration of 0.1 N acetic acid with 0.1 N sodium hydroxide, in which that part of the curve almost parallel to the pH axis is for the most part above pH 7; while in curve III (Fig. 28), representing the titration of 0.1 N hydrochloric acid with 0.1 N ammonium hydroxide, this part is mostly below pH 7. It should be noted that the pH of the solution of the salt formed when an equivalent amount of alkali is added to the acid is very different in these two cases. When both acid and alkali are weak, as when 0.1 N acetic acid is titrated with 0.1 N ammonium hydroxide, there is no part of the curve even approximately parallel to the pH axis (Fig. 28, IV).

The object of an indicator is to show in a rapid and convenient manner when an equivalent amount of alkali or acid has been added, or in other words when the pH of the solution of the salt formed has been reached. Indicators for acids and alkalis are usually organic compounds which exhibit a conspicuous change of colour when the pH of a solution containing them passes over a certain range. This range differs in the case of different indicators, and as a rule does not include the point of absolute neutrality, pH 7. Methyl orange, for example, is red in solutions whose pH is less than about 3, and yellow in solutions whose pH is greater than about 4.4. Phenolphthalein is colourless at pH values less than 8, and pink at pH values greater than about 9.

It is essential, therefore, that the characteristic range of the indicator chosen for a titration must coincide with that part of the titration curve which is approximately parallel to the pH axis, and it should actually contain the pH value of the solution of the salt which is formed when equivalent amounts of the acid and alkali used have been mixed. Since in the case of the titration of a strong acid by a strong alkali, the titration curve is approximately parallel to the pH axis over so wide a range as from 3.5 to 10.0, any indicator whose characteristic range occurred within these limits might be used. Phenolphthalein, however, would show the end-point slightly after the stoichiometric point, while methyl orange would show it slightly before, because these indicators have ranges situated near the limits

of this critical portion of the curve (Fig. 28 I). The most accurate result would be obtained with an otherwise suitable indicator, whose characteristic range actually included the pH of the salt solution formed at the stoichiometric point—in this case about pH 7; *e.g.* bromo-thymol blue (pH range 6-7.6).

It follows from the considerations above that methyl orange would be valueless for the titration of a weak acid, and phenolphthalein for that of a weak base, because in each case the change in colour of the indicator occurs over a range which does not even coincide with the critical part of the titration curve (Fig. 28 II and III).

The titration of a weak alkali by a weak acid cannot be carried out satisfactorily with any indicator, as the change of pH for a small addition of acid near the stoichiometric point is too small to cause a sufficiently sharp colour change in the indicator, even though the range of the latter covers the pH of the solution of the salt formed at the stoichiometric point (Fig. 28 IV).

Because the pH range of colour change of methyl orange occurs at a pH less than 5, this indicator is not much affected by very weak acids such as carbonic acid, boric acid, etc. It is therefore possible to titrate carbonates, borates, etc., of strong bases by means of a strong acid in the presence of methyl orange, as if the strong base alone were present. Sodium borate, for example, acts in such circumstances as if its base were in the form of sodium hydroxide. If, on the other hand, it is desired to estimate sodium hydroxide in the presence of sodium acetate by titration with a strong acid, phenolphthalein must be used, as the use of methyl orange would result in the approximate determination of the total soda.

Conversely, in the estimation of a strong acid such as hydrochloric acid by titration with a strong base in the presence of the salt of a weak base and a strong acid, such as ammonium chloride, it would be necessary to use an indicator such as methyl orange or methyl red, the colour change of which occurs before the pH has risen to the point of liberation of the weak base.

There is available nowadays a large number of indicators covering the whole pH range from 1 to 14. Many of these are unsuitable for ordinary titrations, as their colour change is more or less affected by the presence of salts in solution. Those most satisfactory in general use are described below.

The characteristics of others used in special cases will be given as the occasion arises.

Methyl Orange. pH range, 3.1 (red) to 4.4 (yellow).—Very weak acids have little or no effect on this indicator and it is therefore specially adapted for the titration, with strong acids, of salts of very weak acids such as carbonates, bicarbonates, sulphides, silicates, borates, and arsenites. As carbonic acid is not entirely without influence on methyl orange, it is advisable in the titration of carbonates to expel most of the carbon dioxide when near the neutral point by warming and shaking the solution; the solution must be cooled before completing the titration, as the titration of hot solutions gives somewhat inaccurate results when using methyl orange.

Methyl orange cannot be used for the titration of weak acids. It may be used for ammonia, but methyl red gives a much sharper end-point. Its colour change is not very sharp in solutions as dilute as decinormal.

Methyl Yellow. pH range, 2.9 (red) to 4.0 (yellow).—This indicator is also very slightly affected by weak acids such as carbonic acid, and since it gives a more easily recognisable colour change than methyl orange it is preferable to the latter for the titration of sodium carbonate by strong acids.

Bromo-phenol Blue. pH range, 2.8 (yellow) to 4.6 (blue).—This indicator may be used instead of methyl orange, and is preferable to the latter in artificial light. The colour change passes through a pale green.

Methyl Red. pH range, 4.4 (red) to 6.2 (yellow).—This is the best indicator for the titration of ammonia or for solutions containing ammonium salts. It is more sensitive and gives a much sharper end-point than methyl orange with very dilute solutions of strong acids and alkalis. It is useless for weak acids like acetic acid. It may be used for the titration of soluble carbonates if the solution is heated to the boiling-point. Methyl red is, however, much less sensitive to carbonic acid than litmus or phenolphthalein, and the amount of carbonate present in an ordinary solution of sodium hydroxide is almost without influence on the indicator.

Bromo-thymol Blue. pH range, 6.0 (yellow) to 7.6 (blue).—This is an indicator whose pH range covers the true neutral point. The colour change is sharp. It may be used for the mutual titration of strong acids and strong bases.

Phenolphthalein. pH range, 8.2 (colourless) to 10 (red).—This indicator should be used only with strong alkalis free from carbonate. It is chiefly valuable for the titration of weak acids. Organic acids insoluble in water can be titrated in aqueous alcohol solutions with this indicator. Phenolphthalein must not be used for ammonia or in presence of ammonium salts. With carbonates of the alkalis it indicates “neutrality” roughly at the stage of bicarbonate.

Litmus. pH range, approximately 5.0 (red) to 8.0 (blue).—This indicator is rarely used in solution, owing to its variable composition and behaviour; but in the form of litmus-paper it provides a ready means of distinguishing between acids and alkalis.

Mixed Indicators.—A mixture of certain indicators is useful in special cases where a definite narrow pH range is required. An example of such a mixture is given on p. 102 in the titration of a mixture of hydroxide and carbonate using thymol blue and cresol red.

Universal Indicators.—These are mixtures of indicators so selected as to cover a wide range of pH , showing several changes of colour. They are convenient for showing the approximate pH of a solution, but are not suitable for purposes of a titration, as the colour change is more or less gradual.

Achromatic Indicators.—By mixing a suitable dye with an indicator, a more readily detectable colour change can be produced, especially in artificial light. The effect of the added dye is to reduce that part of the visible spectrum which is transmitted by the indicator both in acid and alkaline solution, thus making a greater contrast in colour between the acid and alkaline solution. The dye should have a colour complementary to that of the indicator at the mid-point of its colour change, and the colour of the dye itself must not be affected by acids or alkalis. Such a mixture gives a grey colour at the transition point, and may be used in titrating turbid or very dilute solutions. For instance, when a blue dye, such as methylene blue, is added to a solution of methyl orange, the mixture is green in alkaline solution. This changes to grey and finally to magenta as the pH falls. The appearance of the grey colour is taken as the end-point of the titration.

In connection with the use of the indicators above, it should be noted that ordinary sodium hydroxide invariably contains

some carbonate, and if a solution of sodium hydroxide is intended for use with more than one indicator it should be standardised separately, using each indicator, and the appropriate value for the normality, corresponding to each indicator, used in subsequent work.

The following instructions summarise the points to be observed in the volumetric estimation of acids and alkalis :—

- (1) For the titration of a strong acid with a strong alkali (free from carbonate) and *vice versa*, any of the common indicators may be used if the concentration of the standard solution is not less than fifth-normal. With more dilute solutions use methyl red, bromo-thymol blue or phenolphthalein.
- (2) For the titration of a weak acid with a strong alkali use phenolphthalein.
- (3) For the titration of a weak alkali with a strong acid use methyl red, methyl orange or bromo-phenol blue.
- (4) For the titration of salts of very weak acids with strong acids use methyl orange or methyl yellow (or in artificial light bromo-phenol blue). Methyl red or bromo-thymol blue may be used for carbonates or sulphides if the titration is carried out at the boiling-point of the solution.
- (5) For the titration of a strong alkali with a strong acid in the presence of a salt of a strong base and a moderately weak acid, use phenolphthalein. The pH of a solution of the salt itself must not be greater than about 8.5.
- (6) For the titration of a strong acid with a strong alkali in the presence of a salt of a strong acid and a moderately weak base, use methyl orange or methyl yellow. The pH of a solution of the salt itself must not be lower than about 4.5.

The titration of a weak acid with a weak alkali, *e.g.* acetic acid with ammonia, is avoided in practice, because no single indicator used in the ordinary way will give a sharp end-point ; and it is not possible to titrate salts of very weak acids with weak acids, *e.g.* sodium carbonate with acetic acid.

For most titrations conical flasks with wide mouths are suitable, or, better still, conical beakers. They should be of resistance glass, as appreciable amounts of alkali are dissolved from ordinary glass, especially by boiling solutions.

The colour change of an indicator is best seen by having a white base (opaque white glass or paper) under the vessel, which should be placed near a window, though not in direct sunlight.

If it is necessary to boil a solution that contains an indicator, the indicator colour may fade. In this case more indicator may be added to the cooled solution.

When the colour change at the end-point is not sharp, as when the solutions are very dilute, it is advisable to prepare a solution for comparison, containing approximately the same concentration of constituents and of indicator as will be present at the end-point of the titration. This solution should be placed beside that which is being titrated, so that the desired tint may be exactly matched, or the slightest difference observed.

Amount of Indicator to be Used

The preparation of indicator solutions is described in the Appendix (p. 516). It is important to note that *they are much more dilute than the solutions usually recommended*. It is a common mistake to use too much indicator, and if only *one* drop of a concentrated solution is required, the addition of a "few drops" represents a large excess. The concentrations recommended in the Appendix are so chosen that approximately 1 ml. of the indicator solution is required for each 50 ml. of liquid present at the end of the titration. One ml. of the indicator can be measured with sufficient accuracy by means of a pipette (Fig. 29) roughly graduated to deliver this quantity.



FIG. 29.

Test Papers.—Books of paper are now available impregnated with a variety of common indicators as well as litmus. Such test papers may easily be prepared by soaking filter paper in the indicator solution, and allowing to dry. These enable the approximate pH of liquids to be determined, as well as merely showing whether they are acid or alkaline.

STANDARD HYDROCHLORIC ACID

(*N* solution contains 36.47 grams HCl per litre)

Standard hydrochloric acid may be obtained (1) by preparing a solution of approximately the desired concentration and then standardising it by one of the methods given below, or (2) by diluting a known volume or weight of "constant boiling-point" acid (see p. 88).

Commercial concentrated hydrochloric acid is usually about 11*N*. Prepare an approximately normal solution of the acid by diluting 90 ml. of the concentrated acid in a measuring cylinder to a litre. Transfer the solution to a bottle and *mix thoroughly* by inverting the bottle several times. Standardise the solution by the following methods:—(1) By means of anhydrous sodium carbonate; (2) by means of borax; (3) by means of potassium iodate; (4) by means of tris(hydroxymethyl)aminomethane.

(1) Standardisation of Hydrochloric Acid by means of Anhydrous Sodium Carbonate

The sodium carbonate required for this purpose must answer the following tests:—

- (1) Dissolve 1 gram in 25 ml. of distilled water; the solution should be perfectly clear. Add dilute nitric acid (free from chloride) in slight excess and then a few drops of silver nitrate solution. No turbidity (or only a *very faint* opalescence) should appear.
- (2) Dissolve 1 gram in 25 ml. of distilled water. Add sufficient dilute hydrochloric acid (about 10 ml.) to make the solution *faintly* acid. Then add about 1 ml. of barium chloride solution, heat until boiling, and set aside until cold. No trace of barium sulphate should be precipitated.

If the sodium carbonate is free from chloride and sulphate and from insoluble impurities, it must next be dried. Heat 3 to 4 grams in a porcelain or platinum crucible to a temperature between 160° and 170° for half an hour in a small air oven, preferably electrically heated to avoid possible contamination by sulphur dioxide from coal gas. If a suitable oven is not

available, support the crucible in a pipe-clay triangle with the wires bent downwards inside a tin, and suspend a thermometer in the sodium carbonate which should be stirred frequently. Allow to cool partially, and transfer while still fairly hot to a clean dry weighing-bottle. Dry sodium carbonate is very hygroscopic.

When the weighing-bottle is perfectly cold, weigh it accurately, shake out from 1 to 1.3 gram of the carbonate into a suitable beaker or conical flask, and weigh again. Shake out a second quantity into another beaker, and reweigh.

Dissolve each portion of carbonate in about 30 ml. of water, add 1 ml. of methyl orange or, better, methyl yellow, and titrate with the hydrochloric acid. Calculate the concentration of the acid as follows :—

1.251 gram Na_2CO_3 required 23.52 ml. acid. Therefore 1 litre of acid is equivalent to $\frac{1.251 \times 1000}{23.52} = 53.17$ grams Na_2CO_3 . But 1 litre of normal acid is equivalent to 53.00 grams Na_2CO_3 . Therefore the acid is $\frac{53.17}{53.00} = 1.003$ N.

The two results should agree to about 2 in 1000.

Sodium bicarbonate, free from chloride and sulphate and insoluble impurities, may be used for the preparation of the normal carbonate. For this purpose, water and carbon dioxide are driven off by heating to a moderate temperature, as in the case of sodium carbonate, in a platinum crucible (or a porcelain basin) for thirty minutes, with frequent stirring.

Accurate results can also be obtained by using pure dry sodium oxalate as the source of sodium carbonate. The former, being sparingly soluble, can be easily purified, and having no water of crystallisation, can be dried by heating to 130° . A suitable quantity is weighed, and then ignited at just below the melting point, preferably in a platinum crucible supported in a hole in an asbestos sheet, until the carbon that separates is burned off. It is thus converted into its equivalent of sodium carbonate.¹ If a porcelain crucible is used it is not possible to burn off all the carbon without some of the sodium

¹ This method is of interest as it enables solutions of acids and alkalis to be linked up with those of potassium permanganate, sodium thiosulphate, etc., through the same standard.

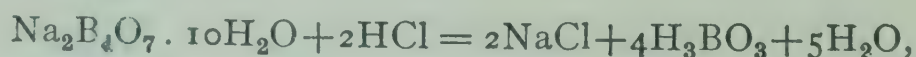
carbonate reacting with the glaze. The bottom of the crucible should be kept at not more than a low red heat for about half an hour, and after cooling, the contents should be extracted with water and the solution filtered. After it has been washed thoroughly, the filter should be burnt and the ash extracted with water, and this extract added to the main solution.

(2) Standardisation of Hydrochloric Acid by means of Borax

In spite of the fact that borax contains water of crystallisation, it has much to recommend it as a standard in acidimetry. It has a high equivalent weight, and the boric acid liberated after neutralisation by a strong acid is so weak that it has no effect on an indicator such as methyl orange, or even methyl red. Further, as it is sparingly soluble in cold water, it can easily be purified by recrystallisation.

Recrystallise a sample of borax by dissolving 15 grams in 50 ml. of hot water. This proportion avoids the formation of crystals above 55° on cooling, and thus prevents the formation of any pentahydrate. Filter the hot solution, and cool the filtrate rapidly. Filter, and free the crystals from mother-liquor by suction. Wash twice with cold water, and then four times with 5 ml. portions of acetone (or with two 5 ml. portions of 95 per cent. alcohol followed by two 5 ml. portions of ether). Spread the crystals in a thin layer on a clock-glass, and allow them to stand at room temperature overnight. Borax is not hygroscopic, but at a temperature slightly over 20° very slowly loses water of crystallisation if the humidity of the air is low. It should therefore be kept in a well-stoppered bottle after the treatment described above.

Borax reacts with hydrochloric acid according to the following equation :—



so that the equivalent weight of borax is $\frac{381.4}{2}$, *i.e.* 190.7.

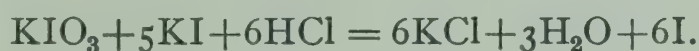
For the standardisation of approximately normal hydrochloric acid, about 4 grams of borax are weighed accurately into a conical flask or beaker, and 100 to 150 ml. of hot distilled

water and 1 ml. of methyl orange or methyl red are added. The acid is run in from a burette, the solution being cooled before the end-point is reached.

If the hydrochloric acid is approximately N/10, methyl red is a more satisfactory indicator than methyl orange. A solution for comparison should be placed alongside (p. 83). For greater accuracy, especially when using methyl red, the solution should be boiled after the indicator just shows a red tint in order to remove small amounts of dissolved carbon dioxide. A further drop or two of acid will then be required to finish the titration.

(3) Standardisation of Hydrochloric Acid by means of Potassium Iodate

Potassium iodate is a reliable substance for use in the standardisation of acids. A known weight of the iodate is added to a solution containing an excess of both potassium iodide and sodium thiosulphate. The subsequent addition of the acid to be standardised liberates its equivalent of iodine according to the following equation :—



The free iodine reacts with the excess of thiosulphate present. As soon as the iodate is completely reduced, the pH of the solution falls sharply, and this can be detected by methyl red, which is added at the beginning of the titration.

(4) Standardisation of Hydrochloric Acid by means of Tris(hydroxymethyl)aminomethane

Tris(hydroxymethyl)aminomethane is readily obtainable, is easily purified and preserved, is almost non-hygroscopic, and has a high equivalent weight. It reacts stoichiometrically with strong acids, and has a negligible indicator correction. Its main disadvantage is that it must be dried under carefully controlled conditions, since it tends to decompose at temperatures above 103°. The indicator recommended is *p*-sulpho-*o*-methoxybenzene-azodimethyl-1-naphthylamine, but good results

can be obtained with ethyl orange. (*Reference* :—Fossum, J. H., Markunas, P. C., and Riddick, J. A., *Anal. Chem.*, 1951, 23, 491.)

Preparation of Standard Hydrochloric Acid Solution from the Constant Boiling-Point Acid

Standard hydrochloric acid can be prepared directly by distillation, followed by dilution to the required strength. This method depends on the fact that when hydrochloric acid is distilled it loses either water or hydrogen chloride, according to the original concentration of the acid, until an azeotropic mixture, of constant composition, distils. The concentration of the constant boiling acid will depend on the barometric pressure during distillation. At a pressure of 760 mm. of mercury, the distillate contains 20.24 grams of hydrogen chloride per 100 grams of liquid.

The density of the constant boiling-point acid distilled at 760 mm. is 1.096 at 25°. It is advisable therefore to start with acid of approximately this density by placing 540 ml. of concentrated hydrochloric acid and 420 ml. of water in a distilling flask attached to a condenser. The diluted acid is distilled and the first 650 ml. of the distillate is collected for ordinary use, and if the boiling-point has become constant, the next 200 ml. of the constant boiling-point acid is collected in a separate receiver.

For very accurate work the distillation should be carried out in apparatus made of Pyrex glass, and back pressure must be eliminated as far as possible by avoiding any constriction in the flow of vapour, *e.g.* the bore of the condenser, etc., should not be less than 6 mm. The rate of distillation should be from 8 to 10 ml. per minute and the distillation must be continuous from the beginning to the end. About 75 per cent. of the acid should pass over before the constant boiling-point fraction, which should consist of the next 10 to 15 per cent., is collected. At least 100 ml. should be left in the distilling flask at the end, and the upper part of the flask must be protected from superheating by supporting the flask on asbestos board with a hole cut in it. The barometric pressure must be read at the beginning and end of the distillation.

The weight of the distillate collected at various atmospheric pressures, which on dilution to a litre will give a normal solution of hydrochloric acid, is shown in the following table :—

Atm. pressure in mm.	Grams of C.B.P. acid containing one mol. of HCl.
770	180.39
760	180.17
750	179.96
740	179.75
730	179.53

In weighing out the required amount of liquid it is convenient to make the final adjustment by means of a capillary tube. If great accuracy is not required, instead of weighing the distillate, 164.2 ml. at 20° C. should be diluted to a litre to give a normal solution if the distillation was carried out at 760 mm. For other pressures 0.2 ml. must be added to or subtracted from this volume for each 10 mm. above or below 760 mm. respectively. The constant boiling-point acid is not hygroscopic or readily volatile, and in a well-stoppered resistance-glass bottle will remain constant in strength for long periods. Although this method takes time it is one of the most accurate for obtaining standard hydrochloric acid.

STANDARD SULPHURIC ACID

(*N* solution contains 49.04 grams H_2SO_4 per litre)

Dilute 30 ml. of ordinary concentrated sulphuric acid by running it slowly into 150 to 200 ml. of cold water contained in a flask. (**Caution.**—The acid must be run into the water, not *vice versa*.) After cooling the solution under the tap, pour it into a measuring cylinder and dilute it to a litre. The solution prepared in this way will be slightly above normal ; the exact concentration must be found by standardisation.

Standardisation.—Sulphuric acid may be standardised in exactly the same manner as hydrochloric acid with weighed quantities of sodium carbonate (see p. 84).

Methyl orange does not give as sharp an end-point with sulphuric as with hydrochloric acid ; methyl red is better.

STANDARD SODIUM HYDROXIDE

(N solution contains 40.00 grams NaOH per litre)

Sodium hydroxide is very deliquescent, and the commercial "sticks" contain varying amounts of carbonate. For most purposes the solution made from ordinary "white sticks" may be used, but when a "carbonate-free" solution is required, it must be prepared by one of the special methods given below.

Weigh about 42 grams of sodium hydroxide on a rough balance. Drop the sticks without delay into a bottle containing about 800 ml. of water. Close the bottle with an ordinary cork or a rubber stopper, and shake gently during the process of solution, otherwise the heat evolved may cause the bottle to crack. Dilute the solution to about 1 litre. (A mark should have been made on the bottle to show this volume.) Allow the solution to cool before standardising it.

Preparation of Carbonate-free Sodium Hydroxide

Sodium hydroxide is often used for the determination of weak acids, with phenolphthalein as indicator. If any carbonate is present, the end-point is not satisfactory. Commercial sodium hydroxide almost invariably contains some carbonate as impurity, and a solution sufficiently free from carbonate for ordinary purposes may be prepared as follows:—Dissolve 200 grams of sodium hydroxide in 250 ml. of water contained in a conical flask. Transfer the solution to a Pyrex bottle or flask with a rubber stopper fitted with a soda-lime tube, and set the vessel aside for a week or longer until the undissolved sodium carbonate has settled. The clear solution is practically free from carbonate, and is about 16.5N. To prepare an approximately normal solution, dilute 61 ml. to 1 litre with CO_2 -free water.

When it is essential to have a solution almost entirely carbonate-free it is preferable to prepare a solution from metallic sodium. The following method may be used, except in the rare cases where the presence of alcohol is not permissible.

Cut away the layer of oxide from the surface of a piece of sodium, using alcohol to lubricate the knife. Weigh out approximately 23 grams of the metal and drop it, in small pieces at a time, into about 50 ml. of ethyl alcohol contained

in a porcelain basin. When the reaction becomes sluggish, it can be hastened by the *cautious* addition of a few drops of water. During the reaction protect the solution from atmospheric carbon dioxide by means of a clock-glass over the basin; and, immediately dissolution is complete, dilute with CO_2 -free water to a litre, and store as described on p. 96. The sodium ethoxide is hydrolysed to sodium hydroxide.

A better, though longer, method for preparing carbonate-free sodium hydroxide from sodium consists in first preparing sodium amalgam by electrolysis of a solution of ordinary sodium hydroxide and subsequent treatment of the amalgam with water free from carbon dioxide.

Fit a cork with three small holes in a 250 ml. round-bottom flask. Into one hole fit a glass tube, in which a short piece of platinum wire is sealed, the tube being long enough to allow the platinum wire to reach the bottom of the flask. Add 30 ml. of mercury, which will cover the platinum wire, and connect the mercury to the negative pole of a six-volt accumulator capable of giving a current of about 2 amperes. The connection is made by adding a little mercury to the glass tube and inserting a copper wire. The second hole in the cork is fitted with a shorter piece of glass tube into which is sealed a short piece of platinum wire, the other end of the wire being welded to a piece of platinum foil about 1 centimetre square. This electrode is connected to the positive pole of the accumulator in a similar manner to the first. The third hole is to allow escape of gas evolved. Now add about 120 ml. of approximately five-normal sodium hydroxide, and adjust the tube carrying the platinum foil so that the latter is just immersed in the sodium hydroxide solution, and well above the mercury surface. The current passing will be about 1.5 amperes, so that allowing for unavoidable losses the electrolysis should be continued for about two and a half hours to yield a tenth of an equivalent of sodium. It is not advisable to make the amalgam more concentrated than will thus have been obtained as a considerable amount of solid would separate. Transfer the amalgam to an evaporating dish, agitate it several times with separate portions of distilled water, and dry it with filter paper.

To make up an approximately decinormal solution of sodium hydroxide, almost fill a Pyrex litre flask (not graduated) with

distilled water and boil this gently for fifteen minutes. Allow this to cool after inserting a stopper with a soda-lime tube attached. When the water has cooled to about 60° add the whole of the amalgam prepared as described above, and replace the stopper with the soda-lime tube. The reaction may be allowed to proceed at the ordinary temperature, but the sodium only reacts slowly. It is therefore better to hasten the reaction by keeping the flask warm. The solution should then be rapidly transferred to the apparatus described on p. 96.

Standardisation of Sodium Hydroxide

The solution must always be standardised. If it is not carbonate-free, methyl orange or bromo-phenol blue must be used as indicator, and the titration carried out with standard hydrochloric acid or sulphamic acid. In the case of carbonate-free sodium hydroxide, phenolphthalein may also be used as the indicator, and instead of standard hydrochloric acid, one of the following organic compounds may be used with advantage :—

	M.-P.	Eq. Wt.	Solubility (g./100g. water).
Succinic acid	187° C.	59.04	6.8 (20°) ; 121 (100°)
Benzoic acid	122° C.	122.12	0.3 (20°) ; 5.9 (100°)
Potassium hydrogen phthalate .	—	204.22	10.2 (25°) ; 36.1 (100°)

These are excellent standards, as they are anhydrous substances, and easily purified.

Oxalic acid and potassium tetroxalate are also used for standardising sodium hydroxide, but they are less reliable, and, as they are hydrated, their purity cannot be checked by melting-point determinations.

A reagent that has recently been recommended as a primary standard in acidimetry is 2 : 4 : 6-trinitrobenzoic acid, which has a high equivalent weight, and is a strong acid.

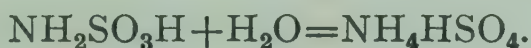
(1) Standardisation of Sodium Hydroxide by means of Standard Hydrochloric Acid

Titrate 25 ml. of the sodium hydroxide solution with standard hydrochloric acid, using as indicator methyl orange

or bromo-phenol blue. If its use with bromo-thymol blue or phenolphthalein is contemplated and the sodium hydroxide solution is not carbonate-free, the titration with these indicators must be carried out at the boiling-point. The value of the normality is calculated separately for each indicator.

(2) Standardisation of Sodium Hydroxide by means of Sulphamic Acid (Aminosulphuric Acid)

Sulphamic acid (Eq. Wt. 97.09) has been recommended as a standard in alkalimetry. It is a white crystalline substance, made by the action of fuming sulphuric acid on urea. It is not hygroscopic and is stable in the solid form below 80°. In solution it is slowly hydrolysed to ammonium bisulphate.



Its solubility is about 18 grams in 100 grams of water at 15°. A dilute solution of the pure substance does not give a precipitate with barium chloride, but some commercial samples give a reaction for sulphate and may also contain urea. Therefore unless the sample is known to be pure it must be recrystallised as follows :—

Heat 120 ml. of water to 75° in a 250 ml. conical flask, add 50 grams of the sulphamic acid and shake the flask until the acid is dissolved, heating gently should this be necessary. Allow the solution to cool with frequent shaking until about one-fifth of the original amount of solid has separated, as will be the case when the temperature has fallen to between 40° and 45°. This solid is discarded as it contains some of the impurities that may be present. Filter at once through a No. 3 sintered glass crucible into a dry filter flask, which has been placed in a bath of water at about 60°. Transfer the filtrate to a dry conical flask and cool it by rotation under the tap, and finally by surrounding the flask with a mixture of ice and water. Filter through a No. 3 sintered glass crucible and wash the crystals once with a little ice cold water, and three times with small portions of acetone. Dry in an oven at 70° to 80° for ten minutes. (*Reference*.—Butler, M. J., Smith, G. F., and Audrieth, L. F., *Ind. Eng. Chem., Anal. Ed.*, 1938, 10, 690.)

(3) Standardisation of Carbonate-free Normal Sodium Hydroxide by means of Succinic Acid

Weigh accurately 1.5 gram of pure succinic acid on a watch-glass, and wash it into a conical flask with freshly-boiled and cooled distilled water. Add 2 ml. of phenolphthalein solution, and titrate with the sodium hydroxide to be standardised.

Example of Calculation.—If 25.62 ml. of a sodium hydroxide solution neutralise 1.4930 gram of succinic acid, 1 litre will neutralise $\frac{1.4930 \times 1000}{25.62}$ grams. But 1 litre of *normal* sodium hydroxide will neutralise 59.04 grams. Therefore the sodium hydroxide solution is

$$\frac{1.4930 \times 1000}{25.62 \times 59.04} = 0.987 \text{ N,}$$

and contains $40.00 \times 0.987 = 39.48$ grams NaOH per litre.

Repeat the experiment with another weighed quantity of succinic acid, and calculate the concentration of the sodium hydroxide solution from the result. The experiment should be repeated until results that agree to 2 in 1000 are obtained.

(4) Standardisation of Carbonate-free Decinormal Sodium Hydroxide

Benzoic acid and potassium hydrogen phthalate are more suitable than succinic acid for standardising decinormal sodium hydroxide, on account of their higher equivalent weight.

Before use benzoic acid should be fused at the lowest possible temperature for about a minute. In this compact state it is non-hygroscopic. Weigh out accurately between 0.3 and 0.4 gram, and transfer it to a 300 ml. conical flask. Add 20 ml. of alcohol, in which it is more soluble than in water, and cork the flask. When the acid has dissolved, add 1 ml. of phenolphthalein solution, and titrate with the sodium hydroxide solution. (1 litre of decinormal NaOH solution will neutralise 12.212 grams benzoic acid.)

Potassium hydrogen phthalate, if not obtainable, is easily prepared by dissolving pure sublimed phthalic anhydride, and slightly more than the calculated weight of pure potassium carbonate to form the acid salt, in water, and mixing the solutions. The acid salt which separates should be purified by recrystallisation from hot water, and dried to a constant weight

at 125°. Weigh accurately about 0.5 gram, dissolve it in water, and titrate with the sodium hydroxide solution, using phenolphthalein as an indicator. (1 litre of decinormal NaOH solution will neutralise 20.422 grams of potassium hydrogen phthalate).

**(5) Standardisation of Sodium Hydroxide by means of
2 : 4 : 6-Trinitrobenzoic Acid**

2 : 4 : 6-Trinitrobenzoic acid has been proposed as a primary standard in acidimetry (Smith, G. F., and Wilkins, D. H., *Anal. Chim. Acta*, 1953, 8, 209). It is a strong acid, has a high equivalent weight, is anhydrous and non-hygroscopic, and is easily purified. The substance is stable at temperatures up to 130°. It has the advantage that it serves as its own neutralisation indicator, there being a colour change from colourless to red at a *pH* of about 8. It is recommended, however, that bromo-thymol blue should be used as indicator. The original paper should be consulted for details of the purification, etc.

**STANDARD BARIUM HYDROXIDE (BARYTA)
SOLUTION**

(N/20 solution contains 7.888 grams $Ba(OH)_2 \cdot 8H_2O$ per litre)

The titration of acids, using phenolphthalein or methyl red as indicator, is accurate only if made with an alkali free from carbonate. Commercial sodium hydroxide always contains carbonate, and even when a pure solution is prepared from sodium and water free from carbon dioxide, it soon becomes contaminated with carbonate by exposure to air. Barium and calcium hydroxide solutions, on the other hand, are easily obtained free from carbonate, since their carbonates are nearly insoluble in water (and still less soluble in solutions of the hydroxides), and if protected from carbon dioxide they form convenient and accurate standard solutions for use with the above indicators.

Preparation of N/20 Baryta Solution.—Dissolve about 35 grams of barium hydroxide [$Ba(OH)_2 \cdot 8H_2O$] in 350 ml. of boiling water contained in a flask, then fit the flask with a cork carrying a soda-lime tube, and set aside until cold. The excess of baryta crystallises, and a clear, saturated solution, which is about 0.35 normal, is obtained.

The standard baryta solution must be kept in a bottle which is permanently connected with a burette, atmospheric carbon dioxide being excluded by means of the soda-lime tubes A and B (see Fig. 30). Pour about 2 litres of water into the bottle

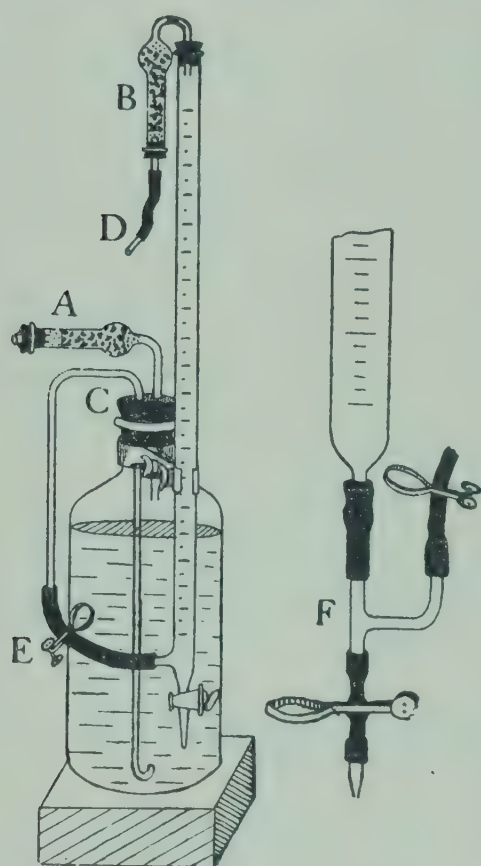


FIG. 30.

(a Winchester quart), and connect it with the burette as shown. Remove the soda-lime tube A and insert, temporarily, a piece of ordinary glass tubing in its place. Attach this tube to the water pump, close the burette tap, and draw a current of air free from carbon dioxide through the burette and bottle for ten minutes. (As the soda-lime tube B is small, more efficient purification of a rapid air-current is secured by attaching temporarily a large soda-lime tower to the tube D.) Replace the soda-lime tube A, lift the cork C, carefully decant the cold baryta solution into the bottle, and replace the cork. Mix the contents of the bottle by drawing a current of CO_2 -free air through the solution, and fill the

burette by opening the clip E and applying suction at D. If the solution is slightly turbid because of a trace of suspended barium carbonate, allow it to stand overnight before drawing it into the burette. The solution is approximately 0.05 normal, and it may be standardised with pure succinic acid, benzoic acid, potassium hydrogen phthalate, or decinormal hydrochloric acid, using phenolphthalein as indicator.

When the burette is not in use it should be kept filled up above the zero mark, and when it is used intermittently the first 5 to 10 ml. run out of the burette are rejected. If a burette

with side-tube is not available, an ordinary burette fitted with a T-piece, as shown at F in Fig. 30, is equally convenient. The burette may be fixed in an ordinary clamp, the Winchester resting on the base of the retort stand; or it may be attached to the bottle by means of an Ostwald burette clamp (Fig. 31).

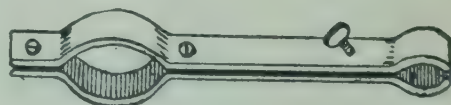


FIG. 31.

STANDARD CALCIUM HYDROXIDE SOLUTION

(N/25 solution contains 1.482 grams $\text{Ca}(\text{OH})_2$ per litre)

A saturated solution of calcium hydroxide is about 0.04 normal. It is made by shaking up excess of freshly slaked lime with water in a Winchester quart bottle, which is then set aside for some days until the solution has become clear. The clear solution is then siphoned into another empty Winchester similar to that used for baryta solution, the carbon dioxide in the burette and bottle having been previously removed by means of a current of purified air.

Calcium hydroxide solution is standardised in the same manner as baryta solution.

ANALYSES INVOLVING THE USE OF STANDARD ACID AND ALKALI**Acetic Acid in Vinegar**

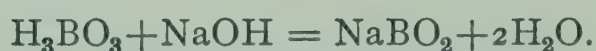
The acidity of a sample of pure vinegar arises almost entirely from acetic acid, and even in adulterated vinegar, other acids are rarely found; the total acidity of the vinegar may therefore be attributed to acetic acid. The concentration of acetic acid in commercial vinegars varies widely but is usually between 4 and 5 grams of acetic acid in 100 grams of liquid. The vinegar, whether coloured or not, is titrated with normal sodium hydroxide using phenolphthalein as indicator.

Dilute the measured quantity of vinegar (25 ml.) with about twice as much water, to diminish the loss of acetic acid by volatilisation. Add 2 ml. of phenolphthalein, and titrate the solution at once with normal sodium hydroxide. The first tinge of pink can be seen even with dark vinegars, but if there is any doubt about the end-point the colour of the solution should be compared with that of the same amount of vinegar diluted to the same extent with water: the colour change is then very readily detected.

Calculate the concentration of acetic acid in grams per litre. It is customary, however, to express the result as the percentage by weight of acetic acid. The density at 15° of 5 per cent. vinegar is about 1.019, and it may therefore be assumed, without serious error, that 1 litre of vinegar weighs 1020 grams. On this basis, calculate the percentage by weight of acetic acid.

Borate in Borax

If a borate is treated with a strong acid boric acid is liberated. If boric acid is titrated with sodium hydroxide, using phenolphthalein as indicator, on account of hydrolysis of the sodium borate the pink colour appears before all the boric acid is neutralised (boric acid is a weak acid). If a polyhydric alcohol such as glycerol or mannitol is added, the *cis*-hydroxy groups of the alcohol unite with the boric acid to produce a complex that behaves like a fairly strong acid which may be titrated in the usual way. The end-point should correspond to complete neutralisation of the boric acid, according to the equation



It is therefore possible to determine boric acid by titration with standard sodium hydroxide if glycerol (free from acid) or mannitol is added before the titration is begun. For the most accurate work it is preferable to neutralise the boric acid to a *pH* between 7.2 and 7.6, add mannitol, and titrate to the same *pH*. The sodium hydroxide used should be standardised empirically against boric acid. (See for example, Blumenthal, H., and Fall, W., *Anal. Chem.*, 1953, 24, 1120.)

Procedure.—Weigh accurately about 3.5 grams of borax, transfer it to a 300 ml. beaker, and dissolve it in about 180 ml. of water. Add 2 ml. of methyl orange, and then dilute hydrochloric acid until the solution is slightly acid. Then run in dilute (about decinormal) sodium hydroxide until the solution is neutral to methyl orange. (The solution now contains sodium chloride and boric acid.) Transfer the solution to a 250 ml. standard flask, dilute to the graduation mark with water, and mix thoroughly.

Determine whether the glycerol that is to be used is neutral. If a 5 ml. sample, to which phenolphthalein has been added, does not give a pink coloration with the first drop of a very dilute (about centinormal) sodium hydroxide solution, take a larger sample, add phenolphthalein, and then sodium hydroxide until a faint pink coloration is obtained. Calculate the correction to be made for the acidity of the glycerol.

To 25 ml. of the prepared boric acid solution, add 15 ml. of glycerol, and titrate with decinormal sodium hydroxide,

using phenolphthalein as indicator. The end-point is reached when the yellowish solution shows a pink coloration. The pink colour should persist on the addition of a little more glycerol; should it disappear, continue the titration until the pink colour is no longer discharged by the addition of more glycerol. The sodium hydroxide must be free from carbonate. If mannitol is used instead of glycerol, 2 to 3 grams are sufficient.

Calculate the percentage of B_2O_3 in the sample of borax and also the corresponding percentage of anhydrous borax, $Na_2B_4O_7$.

Sulphuric Acid in the Concentrated Acid

The concentration of sulphuric acid in the commercial product is usually expressed as the percentage by weight of H_2SO_4 , *i.e.* the number of grams of H_2SO_4 in 100 grams of solution, and it may be very roughly ascertained by finding the specific gravity of the acid and consulting the table given on p. 521. Since the specific gravity of sulphuric acid attains a maximum at about 97 per cent., and varies but little with the concentration above 94 per cent., a more accurate determination of the percentage of H_2SO_4 in a sample of the commercial acid may be made by titration, as follows:—

Weigh accurately in a tared weighing-bottle about 13 grams (about 7 ml.) of the concentrated acid. (Since the acid is hygroscopic, avoid unduly exposing it to the air.) Two-thirds fill a 250 ml. standard measuring-flask with water, and pour in through a funnel as much as possible of the acid. Wash in the remainder by means of a jet of water. Rinse the funnel and remove it. Mix the acid and water thoroughly by imparting a rotary movement to the liquid, and cool under the tap until the liquid is at the room temperature. Dilute to the graduation mark, and mix thoroughly.

Titrate portions of 25 ml. with normal sodium hydroxide, using methyl red or methyl orange as indicator. From the results, calculate the percentage by weight of H_2SO_4 in the original concentrated acid.

Alkaline Earth Metals in Solution as Chloride or Nitrate

METHOD 1.—To the neutral solution of the alkaline earth salt is added an amount of standard sodium carbonate solution

more than sufficient to precipitate all the metal as carbonate. The excess of sodium carbonate remaining is found by titration with standard acid, and the amount used in precipitating the metal obtained by difference.

Exercise.—Measure out 25 ml. of bench barium chloride solution into a 350 ml. flask, dilute to about 100 ml., and slowly run in from a burette 50 ml. of 0.5 N sodium carbonate. Heat to boiling, and maintain the temperature until the barium carbonate has become crystalline and settles rapidly. Cool, make up to 250 ml. in a standard flask, and mix thoroughly. Filter through a dry paper in a dry funnel, and collect the filtrate in a dry receiver, discarding the first few millilitres. Titrate 50 ml. of the filtrate with 0.5 N hydrochloric acid, using methyl orange as indicator. If a correction is applied for the volume of the barium carbonate precipitated, assume its density to be about 4 g./c.c.

METHOD 2.—Neutral solutions of chlorides or nitrates of the alkaline earth metals can be titrated directly by means of standard sodium carbonate using phenolphthalein as indicator. This special use of phenolphthalein with sodium carbonate depends on the sudden rise in pH of the solution when the alkaline earth metal has been precipitated and a slight excess of sodium carbonate is present. Because of the rather slow separation of these carbonates from solution, the pink colour of phenolphthalein appears before the end-point has been reached unless some means of hastening the process is adopted. Heating the solution before titration effects some improvement, but more satisfactory results can be obtained without heating, by adding to the alkaline earth solution an approximately equal volume of acetone, which accelerates the separation of the carbonates.

Measure out 10 ml. of bench barium chloride solution, add 10 ml. of acetone and 1 ml. of phenolphthalein solution. Titrate this, drop by drop, with 0.5 N sodium carbonate until a faint pink colour is permanent throughout the solution for a minute or so.

Similar titrations with reagent calcium chloride or strontium chloride or nitrate may be carried out. (The method is also applicable to solutions of silver and lead salts.)

Mixture of Alkali Hydroxide and Carbonate

METHOD 1.—The total alkali is determined in one part of the mixture, whilst in another part the carbonate is precipitated by adding excess of barium chloride (which must be neutral), leaving the hydroxide still in solution. This is then titrated without filtering off the barium carbonate.

Exercise.—Prepare a mixture of sodium hydroxide and sodium carbonate of known strength by measuring 100 ml. of N/10 NaOH (carbonate free) and 100 ml. of N/10 Na_2CO_3 into a 250 ml. flask, making up to the mark, and mixing thoroughly.

Titrate 25 ml. of this mixture with N/10 HCl, using methyl orange, or better, bromo-phenol blue. This gives the acid equivalent to the total alkali in 25 ml.

Place 50 ml. of the mixture in a conical flask, add 100 ml. of water, and without heating add slowly just a slight excess of barium chloride solution over that required to precipitate the carbonate. This can be done if the concentration of the barium chloride solution is known (see previous Exercise) by calculating the exact volume of barium chloride solution which should be used and adding 1 ml. in excess. Mix thoroughly and allow to stand for a few minutes. Add 1 ml. of phenolphthalein and titrate the hydroxide remaining in solution with N/10 HCl. The acid must be added *very slowly* with constant shaking, especially near the end-point, in order to avoid interaction with the barium carbonate before the phenolphthalein is decolorised. To decrease the risk of this, N/100 acid may be used to finish the titration.

The second titration gives the volume of N/10 HCl equivalent to the original sodium hydroxide in 50 ml., and the difference between the first titration and half the second gives the volume of N/10 HCl equivalent to the carbonate in 25 ml. of the mixture.

If the carbonate content of the mixture is unknown, it is difficult to ascertain when a slight excess of barium chloride has been added. Since the use of a large excess of this reagent leads to low results for the sodium hydroxide, a rough trial must first be made, adding barium chloride equivalent to the total alkali. The second part of the analysis is then repeated, adding, on this occasion, just a slight excess as indicated by the approximate result for the carbonate determination.

METHOD 2.—By titrating with dilute hydrochloric acid in the presence of a suitable indicator, the point at which the hydroxide present has been neutralised and the carbonate converted to bicarbonate can be determined. Both phenolphthalein and cresol red have been used, but these indicators show the colour change too late. On the other hand, a mixture of cresol red and thymol blue shows a colour change very close to the required point. This mixed indicator is prepared by dissolving 0.16 gram of thymol blue and 0.027 gram of cresol red in water containing 4.6 ml. of decinormal sodium hydroxide, and diluting the solution to a litre, 1 ml. being required for each titration. In alkaline solution the colour is blue, and this changes to pale yellow when sufficient acid has been run into the hydroxide and carbonate mixture. The acid must be added slowly, especially near the end-point. The titration is then continued after the addition of methyl orange, or better, bromo-phenol blue, until the change in colour of this indicator shows the complete decomposition of the bicarbonate.

The acid used for the second part of the titration is equivalent to half the total carbonate present, and the difference between the first and second titrations gives the acid equivalent to the hydroxide.

If V_1 = the volume of N/10 HCl required to change the colour of the mixed indicator,
and V_2 = the additional volume of N/10 HCl required to change the colour of methyl orange,

then the weight of Na_2CO_3 in the volume of mixture taken

$$= 2V_2 \times 0.00530 \text{ grams,}$$

and the weight of $\text{NaOH} = (V_1 - V_2) \times 0.00400 \text{ grams.}$

Mixture of Alkali Carbonate and Bicarbonate

Both the methods described above for the analysis of a mixture of alkali hydroxide and carbonate may be used for a mixture of carbonate and bicarbonate, though the first method requires some slight modification.

METHOD 1.—The total alkali is determined by titration with N/10 HCl using methyl orange, or better, bromo-phenol

blue. Before the addition of barium chloride solution to another portion of the mixture, add a known volume of N/10 NaOH, which must be in excess of that required to convert the bicarbonate to normal carbonate, assuming that all the alkali is present as bicarbonate. The procedure of Method 1 for hydroxide and carbonate is now followed.

The calculation is made as follows. The difference between the volume of N/10 NaOH added to the mixture and that found by titration after the addition of barium chloride is equivalent to the bicarbonate originally present. From this and the value obtained for the total alkali present the amount of carbonate can be found.

If V_1 = the volume of N/10 NaOH added to the mixture taken,

V_2 = the volume of N/10 HCl required, after precipitation of the carbonate by BaCl_2 , to change the colour of phenolphthalein,

V_3 = the volume of N/10 HCl required in the titration of another equal portion of the mixture, using methyl orange or bromo-phenol blue as indicator,

then the weight of NaHCO_3 in the volume taken

$$= (V_1 - V_2) 0.00840 \text{ grams,}$$

and the weight of $\text{Na}_2\text{CO}_3 = [V_3 - (V_1 - V_2)] 0.00530 \text{ grams.}$

METHOD 2.—In this case the acid required to change the colour of the mixed indicator (p. 102) is equivalent to half the carbonate, whilst the additional volume of acid required to change the colour of methyl orange or bromo-phenol blue is equivalent to the bicarbonate and half the carbonate.

If V_1 = the volume of N/10 HCl required to change the colour of the mixed indicator,

and V_2 = the additional volume of N/10 HCl required to change the colour of methyl orange or bromo-phenol blue,

then the weight of sodium carbonate in the volume taken

$$= 2V_1 \times 0.00530 \text{ grams,}$$

and the weight of sodium bicarbonate

$$= (V_2 - V_1) \times 0.00840 \text{ grams.}$$

Hydroxide and Carbonate in Lime

(1) Determine the total alkali (hydroxide plus carbonate) as follows :—Weigh accurately about 0.8 gram of the powdered lime, and transfer to a conical flask. Add 25 ml. of normal hydrochloric acid, and warm gently until the lime has dissolved. (A small quantity of insoluble matter usually remains.) Cool the solution, and titrate the excess of acid with normal sodium hydroxide, using methyl orange as indicator. (The colour of the indicator often fades gradually during this titration, and more must be added at intervals.)

(2) Determine the hydroxide as follows :—Weigh accurately about 1.6 gram of the powdered lime, and transfer it to a dry stoppered bottle (200 ml.). Add from pipettes 2 ml. of alcohol and 100 ml. of a 10 per cent. sugar solution, to form soluble calcium sucate. (The alcohol prevents the lime forming lumps when the sugar solution is added.) Shake the bottle more or less continuously for about half an hour. Filter through a dry paper and collect the filtrate (after rejecting the first 5 ml.) in a dry beaker. Titrate 50 ml. of the filtrate with normal hydrochloric acid, using methyl orange as indicator.

From the results obtained in (1) and (2), calculate the percentages of calcium hydroxide and calcium carbonate in the lime. In calculating the former it may be assumed that the volume of the whole filtrate in (2) is 102 ml.

Acidic Radical in Salts of Heavy Metals

A solution of the salt is decomposed by means of hydrogen sulphide whereby an insoluble sulphide is precipitated and an equivalent amount of acid remains in solution ; *e.g.*,



After separation of the insoluble sulphide by filtration, the acid filtrate is titrated with standard alkali. This method is applicable to the determination of the acidic radical in many salts of the heavy metals. It is assumed that no free acid is present in the original solution except that derived from hydrolysis of the salt.

Exercise.—Dissolve about 0.25 gram (accurately weighed) of copper sulphate in hot water, add about 2 grams of pure

sodium chloride, and precipitate the copper with hydrogen sulphide. Filter and wash the precipitate with hydrogen sulphide solution (*cf.* pp. 44 and 413). Boil the mixed filtrate and washings until the hydrogen sulphide is expelled. Cool, and titrate with *decinormal* sodium hydroxide, using methyl red as indicator.

Calculate the percentage of SO_4^{2-} in the salt.

Chloride may be determined in the same way in the case of a copper or mercuric salt.

Aluminium

If sodium hydroxide is run into a neutral solution of an aluminium salt containing phenolphthalein a pink colour develops before an equivalent amount of sodium hydroxide has been added. If the solution is boiled, the pink colour is discharged. On adding more sodium hydroxide and boiling, the colour returns and fades again, and the end-point cannot be reached satisfactorily in this way. It is better to add an excess of sodium hydroxide, boil the solution, and then titrate back with standard acid. Ammonium salts must be absent.

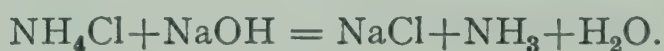
Exercise.—Prepare an approximately 0.2 N solution of alum by weighing accurately about 3.2 grams of the salt, dissolving it in water, and making up to 100 ml. in a standard flask. Measure 25 ml. of this solution into a flask, add phenolphthalein and run in 0.2 N. sodium hydroxide. After running in enough to give a pink colour which lasts for half a minute in the cold, add another 2 ml. of sodium hydroxide and note the total volume used. Boil the mixture for three minutes and, while it is hot, carefully titrate back with approximately decinormal hydrochloric acid until the pink colour is discharged. Boil again for two minutes and the pink colour will probably return because of liberation of carbon dioxide derived from carbonate in the sodium hydroxide. Run in hydrochloric acid drop by drop to discharge the colour and boil again. Repeat this process if necessary until boiling no longer causes a pink colour to develop. Note the total volume of hydrochloric acid required.

Titrate 25 ml. of the sodium hydroxide with the hydrochloric acid, using phenolphthalein as indicator and finish the titration at the boiling-point as described above. From this result

calculate the volume of sodium hydroxide equivalent to the hydrochloric acid used in the above back titration, and the normality and grams per litre of the alum solution from the volume of the sodium hydroxide equivalent to the aluminium.

Ammonia (*Indirect Methods*)

(I) When an ammonium salt, such as ammonium chloride, is decomposed by boiling with an excess of sodium hydroxide solution, ammonia is liberated and an equivalent amount of sodium hydroxide is used up, in accordance with the equation :



If a known quantity of sodium hydroxide (in excess of that required to decompose the ammonium salt) is used, and if, after the decomposition is complete, the residual sodium hydroxide is determined, the difference between these quantities gives the amount of sodium hydroxide equivalent to the ammonium salt taken.

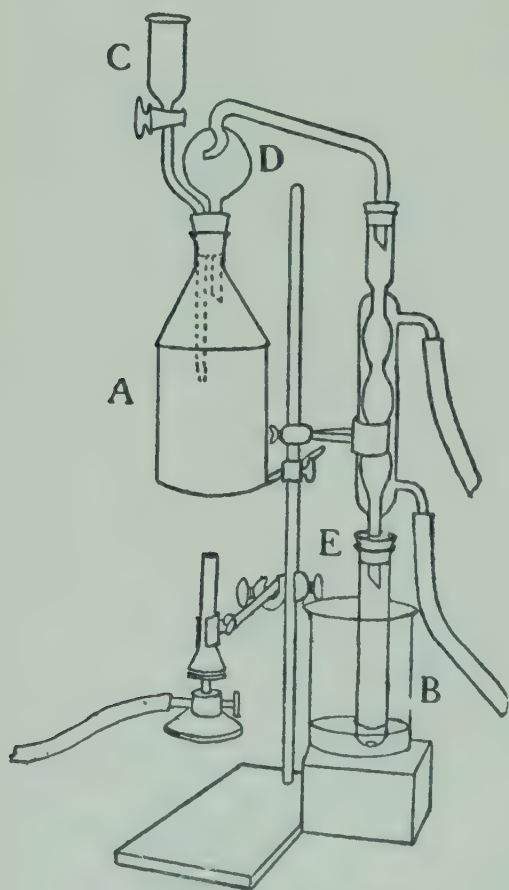


FIG. 32.

If the ammonium salt contains free acid, the solution must be accurately neutralised before adding a measured excess of alkali; or the amount of acid present must be determined by a separate titration and allowed for in the calculation. The ammonium radical in salts like ferrous ammonium sulphate cannot be determined by this method, as part of the sodium hydroxide is used up in the precipitation of the hydroxide of the heavy metal.

Procedure.—Weigh accurately about 1 gram of the substance (*e.g.* ammonium sulphate), wash it into a 250 ml. conical flask, and dilute the solution to about 75 ml. Add a measured

excess (that is an amount which is more than sufficient to decompose the ammonium salt) of normal sodium hydroxide solution (25 ml.) and boil gently to expel the ammonia. At intervals of about five minutes, test for ammonia in the escaping steam with a piece of moist red litmus paper—the test paper being held outside the flask. When the decomposition is complete, *i.e.* when no ammonia can be detected in the steam, cool the solution thoroughly and titrate with standard hydrochloric acid, using methyl red as indicator.

Calculate the percentage of NH_3 in the substance.

(2) Another method makes use of the reaction between formaldehyde and ammonium salts, whereby hexamethylenetetramine is formed, and the acid originally combined with the ammonia is liberated :



Procedure.—Dissolve a weighed quantity of the ammonium salt (*e.g.* 0.4 to 0.5 gram of ammonium sulphate) in water and dilute the solution to 100 ml. in a standard flask. Place 25 ml. of the solution in a conical flask, add 5 ml. of formalin (previously rendered very faintly alkaline to phenolphthalein by addition of sodium hydroxide) and after a few minutes titrate the solution with decinormal sodium hydroxide, using phenolphthalein as indicator.

Ammonia (*Direct Method*)

OUTLINE OF METHOD.—The substance is boiled with excess of sodium hydroxide solution, and the ammonia evolved is absorbed either (*a*) by a known volume of a standard acid solution, and the amount of acid neutralised by the ammonia determined by titration of the excess of acid with standard alkali ; or (*b*) by a saturated solution of boric acid, and titrated directly by standard acid, using an indicator which is unaffected by free boric acid.

METHOD (*a*).—Arrange the apparatus as shown in Fig. 32. A is a copper flask of about a litre capacity. (A round-bottomed resistance-glass flask of about 500 ml. capacity may be used instead of the copper flask.) Fit the flask with a two-holed rubber cork to carry the tap-funnel C and the tube leading to the condenser. Fit a trap¹ at D to prevent any drops of

¹ The trap is more efficient if a hole is made in the *side* of the tube leading from the copper flask into D ; the hole must be situated below the rubber stopper.

sodium hydroxide being driven over during the boiling. Since strongly alkaline liquids tend to bump rather badly when boiling, it is better to pass a current of steam from a separate generator through a glass tube reaching almost to the bottom of the distillation flask, and passing through a third hole in the cork. The steam generator may be another round-bottomed flask fitted with a cork bored with two holes, through one of which passes the tube carrying steam to the distillation flask. The other hole is fitted with a tube almost touching the bottom of the steam generator, the upper end projecting about 8 inches above the cork to serve as a safety valve. This modification of the apparatus is not essential, but it entirely prevents any bumping during distillation of the ammonia. Wet the inner tube of the condenser with water, and attach a boiling-tube with a hole in the bottom. B is a 500-600 ml. beaker. A convenient arrangement is to place B on a wood block, so that the beaker can be lowered or removed by taking away the block.

Examine the apparatus carefully to be sure that there is no leakage at any of the corks. Introduce into the tap-funnel a known quantity¹ of the substance to be analysed, and wash it into the flask with water. In the beaker B place a measured volume (25 or 50 ml.) of normal hydrochloric acid, and add to it an equal volume of water and 2 ml. of methyl red.

When these preparations are completed, run into the large flask through the tap-funnel an excess of sodium hydroxide solution, and close the tap as soon as all the alkali has entered. As a rule about 50 ml. of 2N sodium hydroxide will be sufficient. Add sufficient distilled water (200 ml.) to ensure that the contents of A will not be evaporated to dryness during the experiment.

It is of course essential that all the ammonia evolved should be caught by the standard acid in the absorption flask. The only risk of loss is while the air in the large flask is being expelled. Apply heat therefore, cautiously, so that there is no sudden rush of gas through the standard acid. Boil for thirty minutes. In that time all the ammonia should be over, but it is well to make sure. Disconnect at E, and test the distillate with litmus paper. If it is still alkaline, the boiling must be continued.

¹ In general, the amount of an unknown substance to be taken for analysis must be regulated by the result of a rough quantitative test.

When all the ammonia has been driven over, *open the tap C before extinguishing the flame*, disconnect the apparatus and titrate the solution in B to find how much of the acid remains unneutralised.

In order to avoid overstepping the end-point when titrating the large volume of liquid, proceed as follows:—Transfer about 10 ml. of the liquid in B to a smaller beaker. Run standard alkali into the main portion in B until the neutral point is slightly overstepped. Now add the liquid in the small beaker, and continue the addition of the standard alkali to the end-point. Finally rinse the small beaker into B, and add a further half-drop of alkali if required.

Another Absorption Apparatus.—The apparatus described above for the absorption of the ammonia has the advantage of simplicity, and there is little risk of losing ammonia if the heating is carefully regulated. With the form of absorption apparatus shown in Fig. 33, there is much less risk of losing ammonia. The flask is fitted with a two-holed rubber cork carrying an adapter G for the end of the condenser and a tube H filled with glass beads. At the start of an experiment with this form of apparatus, the measured volume of standard acid is run in through the tube H so as to moisten the beads with acid. One or two drops of methyl red are then poured on the beads; the red coloration produced must persist to the end of the distillation.



FIG. 33.

When all the ammonia has been driven over, the liquid in H is washed down into the flask prior to the titration.

Exercise.—Determine the percentage of NH_3 in ammonium sulphate. Use from 1.3 to 1.5 gram (accurately weighed).

METHOD (b).—The same apparatus is used as in Method (a), but the ammonia evolved is absorbed by about 100 ml. of saturated boric acid, instead of by a fixed quantity of standard acid. This method possesses advantages in that the use of standard alkali is eliminated, and there is no need to measure accurately the volume of boric acid solution used. The weight of ammonium salt taken should not be more than will yield about 0.07 gram of ammonia. The boric acid solution may be made by dissolving 10 grams of pure boric acid in 250 ml. of warm water, and cooling. After the distillation has proceeded for thirty minutes, or until about 100 ml. has passed over, the

absorbed ammonia is titrated with decinormal hydrochloric acid, using methyl orange (or better, bromo-phenol blue) as indicator.

Nitrate

The nitrate is reduced to ammonia by means of (a) Devarda's alloy (Al, 45; Cu, 50; Zn, 5) and sodium hydroxide, or (b) titanous sulphate or chloride and sodium hydroxide. The ammonia is then determined in the usual manner.

Procedure.—(a) Place a weighed portion of the substance (0.3 to 0.5 gram) in a 500 ml. resistance-glass flask, add 100 ml. of water, and 3 grams of Devarda's alloy. This should be in the form of a coarse powder free from fine dust. Use the same apparatus as described under the estimation of ammonia (p. 107).

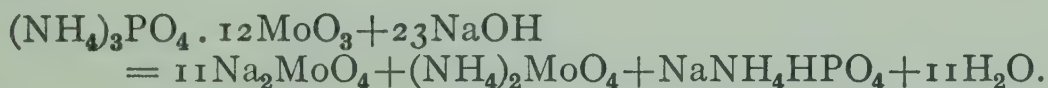
When the apparatus is fitted up and the absorbing liquid ready in the beaker, place about 25 ml. of nearly saturated sodium hydroxide solution (18 grams NaOH dissolved in 20 ml. water) in the tap-funnel, and run about one-third of this into the flask. Warm gently, and add the remaining sodium hydroxide gradually, keeping the reaction under control by cooling the flask with water if necessary. Finally, the contents of the flask are gently heated without boiling for about an hour, because of the danger of carrying over sodium hydroxide spray, after which time the distillation of the ammonia may be carried out by boiling. This is continued for about half an hour, and the ammonia collected is determined as described in the previous experiment.

(b) Place a weighed portion (about 0.15 gram) in the copper or glass flask, and add about 100 ml. of 2 N sodium hydroxide solution. While swirling the contents of the flask, add 25 ml. of commercial titanous sulphate or chloride (15 per cent. solution). Without delay, connect the flask with the condenser, add about 150 ml. of water through the tap-funnel, and distil off the ammonia into the absorbing liquid.

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre). For (a) use about 0.4 gram and collect the ammonia in 25 ml. of normal acid, or in 150 ml. of saturated boric acid. For Method (b) dissolve about 1.5 gram in water and dilute the solution to 250 ml. in a standard flask. Use 25 ml. of this solution and collect the ammonia in 25 ml. of decinormal acid, or in 100 ml. of saturated boric acid.

Phosphate

The phosphate is precipitated as ammonium phosphomolybdate and the precipitate is filtered and washed. It is then treated with a measured volume of standard sodium hydroxide, and the excess of the latter is titrated with standard acid :



From the above equation it may be seen that 1 gram-atom of phosphorus requires 23 gram-molecules of sodium hydroxide, and therefore 1 litre of decinormal alkali is equivalent to 0.1349 gram of phosphorus, or 0.3088 gram of phosphorus pentoxide.

It must be pointed out that the ammonium phosphomolybdate method is subject to numerous disturbing influences. For an account of these see Lundell, G. E. F., and Hoffman, J. I., *Ind. Eng. Chem.*, 1923, **15**, 44.

Procedure.—Place a measured volume of the phosphate solution, containing not more than 10 milligrams of P_2O_5 , in a 400 ml. flask, add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid. Add water to give a volume of about 100 ml. Measure 50 ml. of a freshly prepared 3 per cent. ammonium molybdate solution into another flask. Heat these solutions to between 40° and 45° , and add the ammonium molybdate solution slowly to the phosphate mixture, using a dropping-tube (p. 261), and shaking continuously. It is important not to heat the solutions over 45° , in order to avoid contaminating the precipitate with molybdic acid.

The flask is now fitted with a rubber stopper, shaken vigorously for five minutes, and left to stand for half an hour. Filter through paper pulp on a 1 cm. perforated porcelain disc (p. 45). Transfer the precipitate to the filter, and wash the flask and the precipitate with 1 per cent. potassium nitrate solution until the filtrate is not acid to methyl orange. This will require about 100 ml. of washing liquid. Now return the precipitate together with the paper pulp and porcelain disc to the flask in which the precipitation was carried out. Add from a pipette 50 ml. of decinormal sodium hydroxide free from carbonate, which will be more than enough to dissolve the yellow precipitate completely. The alkali must be added

through the funnel in which the filtration took place, in order to dissolve the precipitate which remains on the sides, and the funnel must be rinsed into the flask with distilled water.

Shake the flask until all the yellow precipitate is dissolved, add phenolphthalein, and titrate with decinormal hydrochloric acid until the pink colour is completely discharged.

Exercise.—Determine the percentage of P_2O_5 in microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$. (This is a more reliable standard than potassium dihydrogen phosphate, which is often used. If it is to be recrystallised, a little ammonia should be added to replace that lost when the solution is hot.) Weigh accurately between 0.2 and 0.25 gram of microcosmic salt, dissolve it in water, and dilute to 250 ml. in a standard flask. Mix thoroughly, and use 25 ml. for each determination.

Determination of Phosphorus in Iron.—Place a weighed quantity of the metal (about 2 grams of steel or 0.4 gram of cast iron) in a covered 300 ml. beaker, add 30 ml. of water and 10 ml. of concentrated nitric acid, and warm on a hot-plate until the metal has dissolved. Add 30 ml. of decinormal potassium permanganate solution and boil for three minutes to destroy carbides and complete the oxidation of the phosphorus. The boiling must be continued until the pink colour disappears. Then add enough ferrous sulphate solution (containing sulphuric acid) to dissolve the precipitated manganese dioxide. Boil the solution to expel oxides of nitrogen. Rinse the cover-glass and add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid and filter if necessary. Precipitate the phosphate at 40° to 45° by adding 50 ml. of ammonium molybdate solution, and complete the determination by the alkalimetric method described above. In this case, however, the precipitate must first be washed with 0.1N nitric acid until free from iron, and then with 1 per cent. potassium nitrate solution until free from acid.

From the data obtained, calculate the percentage of phosphorus in the sample.

In the case of a high-chromium or stainless steel, dissolve 2 grams of the sample in 20 ml. of 60 per cent. perchloric acid in a 500 ml. conical flask, warming to effect dissolution. Boil for thirty minutes, with a small funnel in the mouth of the flask, to ensure complete oxidation. Cool the deep red solution, dilute to 100 ml., and add ammonium hydroxide of

0.9 sp. gr. (p. 523) until a slight precipitate is formed. Dissolve this by the addition of about 20 ml. of nitric acid of 1.2 sp. gr. (p. 522). Add a few ml. of 10 per cent. ammonium bisulphite solution to reduce the chromate present. Boil to remove nitrous fumes and free chlorine, add 10 grams of ammonium nitrate and 5 ml. of concentrated nitric acid, filtering if necessary, and precipitate the phosphate as described above.

Persulphate

Some persulphates can be determined by boiling their aqueous solutions and titrating the sulphuric acid set free :



The decomposition, which is slow even at the boiling-point, can be accelerated by the addition of a solution of silver nitrate.

Weigh accurately between 0.3 and 0.4 gram of the sample of potassium persulphate, and dissolve it in 100 ml. of water. Add methyl red and if the solution is acid owing to the presence of some bisulphate, run in decinormal sodium hydroxide until it is neutral. Then add about 10 ml. of decinormal silver nitrate, and boil for not less than ten minutes. Cool, again add methyl red, and titrate with decinormal sodium hydroxide.

Ammonium persulphate does not give accurate results by this method, because some nitric acid is formed owing to partial oxidation of the ammonium radical. For a better method, see p. 129.

Reduction - Oxidation Processes

OXIDATION and reduction necessarily occur together, one substance being oxidised as another is reduced. The theory of these reactions is dealt with under Electrometric Methods on p. 217. Reactions described as oxidations are usually those in which the oxidising agent forms the standard solution, whilst in those classified as reductions a standard solution of the reducing agent is employed.

A considerable number of reagents are used in the form of standard solutions. The following table contains those usually employed :—

Oxidising Agents.	Reducing Agents.
Potassium permanganate.	Sodium thiosulphate.
Potassium dichromate.	Arsenious acid.
Ceric sulphate.	Titanous sulphate.
Iodine.	Ferrous sulphate.
Potassium bromate.	
Potassium iodate.	

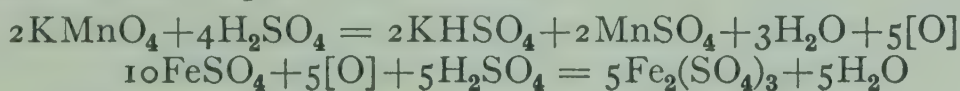
When using reagents such as potassium permanganate, which are deeply coloured themselves but give colourless solutions after reacting, no indicator is required. In other cases some additional substance must be added which will serve as an indicator. The theory underlying the use and action of a reduction-oxidation indicator will be dealt with later (p. 220).

STANDARD POTASSIUM PERMANGANATE

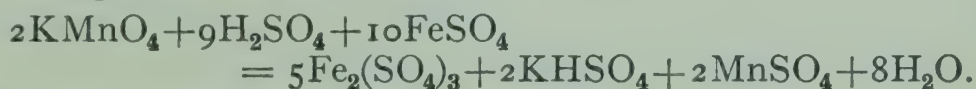
(N/10 solution contains 3.161 grams $KMnO_4$ per litre)

Nearly all of the determinations commonly made with potassium permanganate are carried out in an acid solution. Hydrochloric acid is usually avoided if iron is present, because it may be oxidised by the permanganate (see p. 135), and since nitric acid, like the permanganate, is an oxidising agent, its presence is not desirable. Sulphuric acid is the most suitable acid, and it is almost always added in titrations that are to be carried out with permanganate in an acid solution.

Potassium permanganate in presence of sulphuric acid oxidises ferrous sulphate as follows :—



or, combining these equations,



The first equation shows that two molecules of the permanganate provide five atoms of available oxygen. A solution that contains one-fifth of the molar weight per litre will provide 8 grams of oxygen per litre and is described, therefore, as a normal solution. A decinormal solution contains one-fiftieth of the molar weight per litre, *i.e.* 3.161 grams.

Standard solutions of potassium permanganate should be prepared from a well-crystallised specimen of the salt, in the form of brilliant black crystals with a metallic lustre, free from any blue or violet iridescence. A solution prepared from the pure salt and water free from organic matter is very stable, but the salt of commerce (including some brands described as “for analysis”) usually contains a small quantity of manganese dioxide, and this impurity brings about progressive decomposition of the solution, slowly at first and afterwards more rapidly. If the suspended oxide is completely removed by careful filtration, the solution will remain unchanged for many months if kept in the dark.

Weigh about 3.2 grams of potassium permanganate. Transfer the crystals (which must not be powdered) to a clean flask and add about 500 ml. of cold distilled water. Shake the flask at intervals and set it aside overnight. Filter the solution through a funnel containing a plug of glass-wool covered with a little asbestos into a filter-flask, and dilute to the mark in a graduated litre flask with freshly boiled and cooled distilled water. Transfer the solution to a thoroughly clean, glass-stoppered bottle. (The flasks and bottle must first be cleaned with chromic acid solution and afterwards rinsed with distilled water.)

More certain removal of manganese dioxide will be accomplished by filtering through a No. 4 sintered glass crucible (p. 238). This can be carried out automatically by fitting a rubber bung just into the top of the crucible. A glass tube bent twice at right angles passes through the bung so that

the end is almost touching the glass filter, thus preventing any possibility of the solution coming into contact with the rubber. The other end of the tube dips into the flask containing the permanganate. Since it is very difficult to draw air through a wet No. 4 sintered glass filter, this must either be dry, or enough of the liquid to be filtered must be added to ensure the liquid in the flask being drawn over. By the use of a screw-clip on the tubing between the filter flask and the pump, or an intermediate tap, the water may be turned off after a partial vacuum has been established.

Since the meniscus cannot be clearly seen through the deep purple solution (unless it is very dilute), the burette readings are taken at the highest level of the liquid surface which, against a white card, appears as a sharp, horizontal line. A burette that has been used for permanganate solution should be emptied and cleaned immediately after use. Brown stains of manganese oxides can be removed with sulphurous acid, or with acidified ferrous sulphate.

As already explained, most permanganate titrations are carried out in presence of sulphuric acid, and sufficient acid must be added—*before beginning the titration*—to prevent the formation of a permanent brown coloration or a brown precipitate. The permanganate solution must be run in slowly, with continuous stirring or very frequent shaking. No indicator other than the permanganate itself is required, and the end-point of the titration is easily recognised. A single drop of decinormal permanganate solution is sufficient to impart a distinct pink colour to 200 ml. of water. An endeavour should be made to keep the volume of the solution at the end-point of all titrations as nearly constant as possible—in general, about 100 ml.—in order that a constant excess of permanganate will be required to give the same intensity of pink colour. Greater accuracy will thereby result.

Permanganate solutions may be standardised with arsenious oxide or sodium oxalate, both of which are obtainable as “analytical reagents” of a definite standard of purity.

Standardisation with Arsenious Oxide.—For accurate results with this standard the presence of a suitable catalyst is necessary, a trace of potassium iodide or iodate being usually employed. Osmium tetroxide may also be used as a catalyst, but it is a dangerous substance.

Weigh out accurately into a 400 ml. beaker about 0.2 gram of pure dry arsenious oxide, As_2O_3 (see p. 175), and add about 10 ml. of a 20 per cent. solution of pure sodium hydroxide. Stir until the solid has dissolved, add 100 ml. of water, 10 ml. of concentrated hydrochloric acid, and *one* drop of a 0.05 per cent. potassium iodide solution. Titrate with potassium permanganate, which must be added drop by drop near the end, allowing the colour to disappear completely before the next drop is added. The reaction is finished when the pink colour persists for thirty seconds.

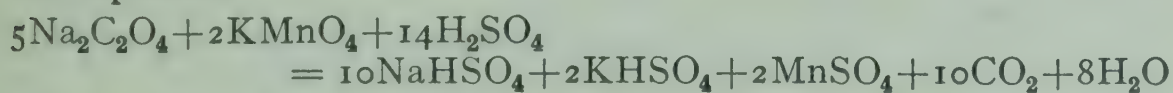
From the reading obtained, deduct the volume of potassium permanganate required to give the same depth of colour to the same final volume of liquid containing the same amounts of sodium hydroxide, acid, and catalyst.

The gram equivalent of arsenious oxide is 49.46.

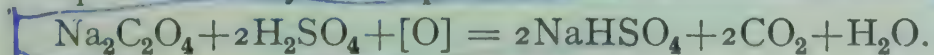
Standardisation with Sodium Oxalate.—Sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$, is an anhydrous salt, and it may be dried before use by heating in an air-oven for an hour at 105° .

Weigh accurately from 0.17 to 0.19 gram of the salt. Wash it into a conical flask, add 30 ml. of dilute sulphuric acid, and dilute to about 70 ml. Heat the solution to about 90° (just short of boiling). Titrate the hot solution by running in the permanganate *very slowly*, while shaking the flask continuously. See that the temperature does not fall below 60° , and allow each drop (or half-drop) of permanganate to become completely decolorised before adding the next. A very faint, permanent pink coloration marks the end-point. (The formation of a brown precipitate or a permanent brown coloration during the titration indicates that the solution is too cold, or that the permanganate has been added too quickly, or that insufficient sulphuric acid is present.) Repeat the titration with another weighed portion of the sodium oxalate.

The oxidation of sodium oxalate by potassium permanganate in presence of sulphuric acid may be represented by the equation



or in simpler form by the equation



It may be seen from the second equation that 1 molar weight of sodium oxalate (134.0 grams) requires 16 grams of oxygen.

Therefore 67.0 grams of sodium oxalate require 8 grams of oxygen, or 1 litre of normal permanganate solution.

Alternative Method of Standardisation with Sodium Oxalate.—The customary method given above for standardising potassium permanganate by sodium oxalate in hot acid solution has been shown (*J. Res. Nat. Bur. Stan.*, 1935, **15**, 493) to give a value for the normality which is about 0.4 per cent. higher than that obtained using arsenious oxide or standard ferrous solutions. The following procedure gives results which agree closely with those obtained when these other standards are used.

Weigh accurately about 0.3 gram of sodium oxalate, which has been dried at 105°, into a 600 ml. beaker. Add 250 ml. of a solution of sulphuric acid prepared by adding 15 ml. of concentrated sulphuric acid to 285 ml. of water, boiling for ten minutes and cooling to $27^{\circ} \pm 3^{\circ}$. After the oxalate has dissolved, add 40 ml. of the approximately N/10 potassium permanganate, running in about 30 ml. per minute with gentle stirring, keeping the temperature at about 27°. When the pink colour has disappeared, heat to between 55° and 60°, and run in the potassium permanganate until a very faint pink colour persists for half a minute, adding the last millilitre slowly, allowing the colour from each drop to disappear before the next is added. It is advisable to carry out a "blank" experiment, omitting the sodium oxalate, and working to approximately the same depth of colour at the end-point.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE

Iron

One of the most important determinations that can be made by means of a standard solution of potassium permanganate is that of iron (p. 135). Iron can be determined, however, equally well with standard potassium dichromate, and all the examples of analysis involving the determination of iron are given after the preparation and use of a standard dichromate solution have been described (see p. 131).

Oxalic Acid and Oxalates

The procedure is described under the standardisation of permanganate with sodium oxalate (p. 117).

Peroxides

Hydrogen Peroxide.—In presence of sulphuric acid, hydrogen peroxide and potassium permanganate solutions interact as follows :—



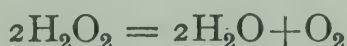
The decomposition of the hydrogen peroxide may be represented more simply by the equation



which shows that 17.01 grams of hydrogen peroxide require 8 grams of oxygen, or 1 litre of normal permanganate.

The concentration of commercial hydrogen peroxide may be determined as follows :—Dilute 10 ml. of the solution to 250 ml. in a standard flask. After mixing, measure 25 ml. into a conical flask, and dilute to about 300 ml. Add 25 ml. of dilute sulphuric acid, and titrate with decinormal permanganate.

The commercial practice is to express the concentration of hydrogen peroxide solutions in terms of the volume of oxygen obtainable from them on decomposition by heat. Thus "ten volume" hydrogen peroxide refers to a solution of which 1 ml. will yield 10 ml. of oxygen. It should be observed that the decomposition of hydrogen peroxide by heat,



liberates only half the quantity of oxygen obtainable by oxidation with permanganate.

From the result obtained in the titration, calculate the concentration of the original solution (1) as grams of H_2O_2 per litre, (2) in terms of the oxygen value, assuming the oxygen to be measured at N.T.P.

If organic preservatives are present, a more accurate result will be obtained by the method on p. 172.

Barium Peroxide.—When barium peroxide is treated with very dilute hydrochloric acid, the hydrogen peroxide formed may be titrated with standard potassium permanganate as in the determination above. The use of sulphuric acid is inadvisable in this case as the barium peroxide may become coated with insoluble sulphate. Hydrochloric acid is permissible, as appreciable amounts of iron are not likely to be present (see p. 135).

Weigh out accurately about 0.2 gram of barium peroxide, and transfer it to a conical flask. Add about 300 ml. of water, and then about 30 ml. of dilute hydrochloric acid. Shake gently until the peroxide is dissolved, and titrate the liberated hydrogen peroxide with decinormal potassium permanganate.

The formation of hydrogen peroxide takes place in accordance with the equation



so 5BaO₂ will be equivalent to 2KMnO₄.

Peroxides of zinc, magnesium, calcium, and sodium, and sodium perborate which also yields hydrogen peroxide on treatment with acids, may be determined by dissolving about one-four hundredth of their equivalent weight in about 100 ml. of *cold* dilute sulphuric acid with continuous stirring. The solution obtained is then titrated with decinormal potassium permanganate.

Dioxides

Manganese Dioxide (Pyrolusite).—The dioxide is boiled with excess of oxalic acid and dilute sulphuric acid until the reaction is complete. Part of the oxalic acid is oxidised by the dioxide and the residual portion is determined by titration with standard permanganate. The equation is



Prepare an approximately 0.2N solution of oxalic acid by dissolving about 3 grams of the crystals in 250 ml. of water. Dilute 10 ml. of this solution to 50 ml., add 25 ml. of dilute sulphuric acid, and titrate (at 70° to 80°) with standard permanganate.

Weigh accurately about 0.4 gram¹ of *finely powdered*² pyrolusite in a small weighing tube (small test-tube). Transfer the pyrolusite to a conical flask (about 250 ml.) and reweigh the tube. Measure 50 ml. of the oxalic acid into the flask, add 25 ml. of dilute sulphuric acid, place a small funnel in the mouth of the flask, and boil gently until no black particles remain undissolved. (A small residue of silica is usually present.) Add water to replace that lost by evaporation, and titrate (at 70° to 80°) with standard permanganate.

¹ If it is probable that the sample contains less than 75 per cent. of manganese dioxide, a larger quantity should be taken.

² It is imperative that the sample be very finely powdered.

Calculation.—0.4084 gram of pyrolusite was boiled with 50 ml. of an oxalic acid solution. The residual oxalic acid required 24.60 ml. of 0.1025N permanganate. Also, 10 ml. of the oxalic acid solution required 21.20 ml. of the permanganate, and therefore 50 ml. requires 106.0 ml. Therefore the MnO_2 is equivalent to $106.0 - 24.60 = 81.40$ ml. of 0.1025N permanganate.

From the equation it may be seen that MnO_2 is reduced to manganous sulphate, corresponding to MnO , and 43.46 grams MnO_2 yield 8 grams of oxygen. One ml. of normal permanganate therefore corresponds to 0.04346 gram MnO_2 . The percentage of MnO_2 in the sample is therefore

$$\frac{81.4 \times 0.1025 \times 0.04346 \times 100}{0.4084} = 88.9.$$

Lead Dioxide and Red Lead.—For the determination of lead dioxide by a method similar to that described above for manganese dioxide, the use of sulphuric acid is not satisfactory owing to the insolubility of lead sulphate. If nitric acid is used instead of sulphuric acid, a little oxalic acid may be decomposed by the nitric acid, while the titration of the excess oxalic acid is very slow. The use of perchloric acid avoids these difficulties.

Weigh accurately about 0.3 gram of lead dioxide (PbO_2), or about 0.6 gram of red lead (Pb_3O_4), into a conical flask. Add 25 ml. of 0.2N oxalic acid solution, 100 ml. of 20 per cent. perchloric acid, and heat on a water-bath until the oxide has dissolved. Add 150 ml. of water, heat to 80° , and titrate with standard potassium permanganate.

Nitrite

The oxidation of a nitrite to a nitrate by potassium permanganate in presence of sulphuric acid is shown by the equation



The oxidation is essentially represented by the equation



The molar weight (85.1 grams) of potassium nitrite requires 16 grams of oxygen, and therefore 42.55 grams require 1 litre

of normal permanganate. The oxidation must be carried out in such a manner as to avoid the loss of nitrous acid that would occur if the nitrite solution were made acid before the permanganate is added.

Procedure.—Prepare a standard (approximately decinormal) solution of oxalic acid by dissolving about 1.5 grams of the crystals in 250 ml. of water and titrating 25 ml. of the solution with decinormal permanganate in the usual way.

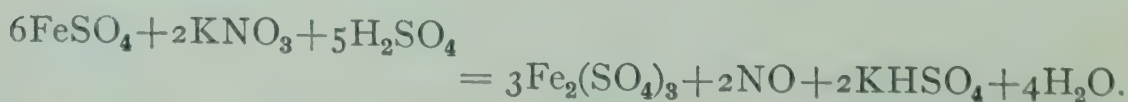
Determine the percentage of potassium nitrite in a sample of the commercial salt. Weigh accurately from 1 to 1.2 grams of the nitrite, dissolve in cold water and dilute to 250 ml. in a standard flask.

Make a preliminary titration of the nitrite solution to find out the approximate amount of potassium permanganate which is required to oxidise a measured volume of it :—Dilute 10 ml. of the nitrite solution to about 100 ml. in a conical flask and warm to about 70°. Add 5 ml. of dilute sulphuric acid and run in standard permanganate until a permanent, decidedly pink coloration is obtained. Note the volume required. An accurate determination is then made as follows :—

Measure into a conical flask not less than three times the volume of standard permanganate required in the preliminary titration, *i.e.* more than sufficient to oxidise 25 ml. of the nitrite solution. Add 25 ml. of dilute sulphuric acid, dilute to 200 ml., and warm the solution to about 50°. Run 25 ml. of the nitrite solution slowly into the excess of permanganate, with continuous shaking, and then add 10 ml. of concentrated sulphuric acid and heat the mixture to about 80° to complete the oxidation. To the hot solution add (from a burette) a measured excess of standard oxalic acid (sufficient to decolorise the solution), and titrate the excess of oxalic acid with standard permanganate.

Nitrate

When a solution of ferrous sulphate is boiled with a nitrate and excess of sulphuric acid, the ferrous sulphate is oxidised and nitric oxide is set free :



If, therefore, a known quantity of ferrous sulphate is taken,

the amount of nitrate present can be calculated from the amount of ferrous sulphate that becomes oxidised in the process. Air must be carefully excluded during the process, more especially as nitric oxide and oxygen form nitrogen peroxide which would then oxidise more of the ferrous sulphate. The air is accordingly displaced by a current of carbon dioxide. The mixture must contain from 35 to 40 per cent., by volume, of concentrated sulphuric acid.

The apparatus is shown in Fig. 34. It consists of a 400 ml. conical flask, fitted with a reflux condenser, and provided with a tube A, through which the carbon dioxide enters. A U-tube, containing a little water, is attached to the top of the condenser. The carbon dioxide is supplied from a Kipp generator. If the generator has been freshly charged, the air must be carefully displaced before using the gas.

Procedure.—Prepare a solution of ferrous sulphate by dissolving about 7 grams of the crystals in cold water mixed with 10 ml. of dilute sulphuric acid and dilute the solution to 250 ml. Titrate 25 ml. of the solution with decinormal permanganate.

Weigh accurately 1.2 to 1.3 grams of the nitrate, dissolve in water, and dilute the solution to 500 ml. in a standard flask. Measure 25 ml. of the solution into the conical flask, and add 25 ml. of the ferrous sulphate solution. Connect the flask with the condenser, and pass a rapid current of carbon dioxide through the apparatus for five minutes. Then, without interrupting the current of carbon dioxide, immerse the flask in cold water, remove the U-tube, and slowly introduce, through the condenser, 30 ml. of concentrated sulphuric acid. Replace the U-tube, and reduce the amount of carbon dioxide entering the flask until about one bubble of gas per second passes through the water in the U-tube. Boil the contents of the flask for ten minutes. Increase the rate of the carbon dioxide again, and cool the solution by immersing the flask in water. Detach the flask and rinse the carbon dioxide inlet-tube into it. Dilute the solution to about 150 ml., and titrate the residual ferrous sulphate with decinormal permanganate.

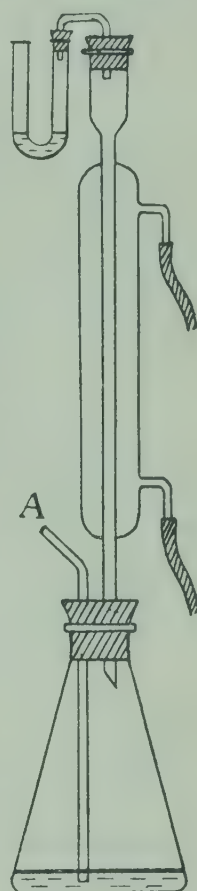


FIG. 34.

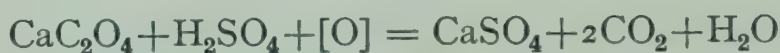
One ml. of normal permanganate corresponds to 0.02834 gram NaNO_3 .

Exercise.—Determine the percentage of sodium nitrate in a sample of the commercial salt (Chili nitre).

Calcium

The calcium is precipitated as calcium oxalate. The washed precipitate is dissolved in sulphuric acid and the solution is titrated with standard permanganate.

From the equation



it may be seen that the molar weight of CaC_2O_4 (containing 40.08 grams Ca) requires 2 gram-equivalents of oxygen. Therefore 1 ml. of normal permanganate corresponds to 0.02004 gram Ca.

Exercise.—Weigh accurately about 0.15 gram of powdered calcspar. Transfer it to a 300 ml. beaker, add 10 ml. of water and 5 ml. of dilute hydrochloric acid, and cover the beaker with a clock-glass. Warm until the calcspar has dissolved, then dilute with a little water and boil the solution for a few minutes in order to free it from carbon dioxide. Rinse the clock-glass into the beaker and add a few drops of methyl red and then ammonia until the solution is neutral. Add 5 ml. of dilute hydrochloric acid, dilute the solution to about 150 ml., heat until boiling, and add drop by drop about 15 ml. of a hot solution of ammonium oxalate. Use a 2 per cent. solution freshly prepared from the solid. (Old solutions contain some carbonate, especially if they have been kept in sunlight.) Now add ammonia drop by drop until alkaline, stirring continuously to avoid “bumping,” and boil for a few minutes. This procedure gives a coarse-grained precipitate which is easily filtered off and washed. Allow the precipitate to settle, and then make sure that precipitation is complete by adding a few more drops of the reagent. Place the beaker on the steam-bath for one hour.

Decant the supernatant liquid through a 9-cm. paper, wash the precipitate once by decantation, and then transfer it to the filter (see p. 43). Wash the precipitate and filter paper with water containing a little ammonia (25 ml. of 2N ammonia

diluted to 100 ml.), until the washings give no opalescence with nitric acid and silver nitrate. (Always rinse the end of the funnel stem before collecting a portion of the washings—about 5 ml.—for a test like this.) It is better to complete the washing with a saturated solution of calcium oxalate after most of the ammonium oxalate has been removed.

Now place the beaker in which the precipitation was made under the funnel, pierce the apex of the filter paper with a *pointed* glass rod, and wash the precipitate into the beaker with hot water. Pour about 25 ml. of hot dilute sulphuric acid into the filter, in small portions at a time, taking care that the acid comes into contact with every part of the paper and that some of it is poured behind the double fold of the paper in case any of the calcium oxalate has lodged there. Then wash the paper thoroughly with hot water. Heat the calcium oxalate solution to about 90° , and titrate with standard permanganate.

Calculate the percentage of calcium in the calcspar.

Lead

The lead is precipitated as lead oxalate by the addition of excess of ammonium oxalate in the presence of acetic acid, and it can be determined either by titration of the excess of the ammonium oxalate or by treatment of the lead oxalate with hot dilute sulphuric acid, followed by titration of the oxalic acid formed. The back titration method is often preferred because of the low solubility of the lead sulphate formed in the second method, with the possibility of this lead sulphate enclosing some unattacked lead oxalate. Both methods are satisfactory, and it is also possible to use hydrochloric acid for decomposing the lead oxalate. This acid gives a clear solution when hot, ensuring complete attack, but it must not be more concentrated than 0.5N or it will be oxidised by the permanganate.

Exercise.—Weigh accurately about 1.5 gram of lead nitrate, dissolve it in water and make up the solution to 100 ml. Prepare also an approximately N/5 solution of ammonium oxalate by dissolving about 1.4 gram in 100 ml., and if the first method is to be used titrate two 10 ml. lots of this with standard potassium permanganate.

METHOD 1.—Measure 25 ml. of the lead nitrate solution into a beaker, add about 25 ml. of water and 5 ml. of dilute acetic acid. From a pipette run in 25 ml. of the ammonium oxalate solution, heat to boiling and allow to cool. Transfer the whole contents of the beaker through a funnel to a 100 ml. graduated flask, rinsing into the flask with several small amounts of water, and finally making up the volume to 100 ml. Filter through a dry filter into a dry vessel, rejecting the first few millilitres of the filtrate. Titrate 25 ml. of the filtrate with potassium permanganate. Calculate the excess of ammonium oxalate in the 100 ml. of the filtrate, and thence the volume of ammonium oxalate used in precipitating the lead, and the weight of lead nitrate taken for analysis.

METHOD 2.—Precipitate the lead as oxalate as described above, but for this method it is not necessary to add more than about 15 ml. of the ammonium oxalate solution. After cooling decant the supernatant liquid through a filter, wash by decantation, once with water, and twice with a saturated solution of lead oxalate, prepared by shaking a little of the solid with water at frequent intervals and filtering. Transfer the precipitate to the filter and wash with the lead oxalate solution until a few millilitres of the filtrate do not give a turbid solution with four drops of the original lead nitrate solution. Treat this precipitate exactly as described for the determination of calcium, but use hot 4N sulphuric acid instead of the ordinary dilute acid.

As an alternative to attacking the lead oxalate with sulphuric acid use approximately 25 ml. of dilute hydrochloric acid, and wash the filter paper with about 75 ml. of hot water, giving a final concentration of hydrochloric acid of about 0.5N. Heat to between 60 and 70°, at which temperature the lead chloride formed will be in solution, and titrate with potassium permanganate. At the end-point the colour due to half a drop of permanganate in excess should be permanent for at least a minute.

Manganese

The following method is based on the fact that a manganous salt is oxidised to permanganic acid by sodium bismuthate in presence of acid. The permanganic acid is determined by adding a known excess of ferrous sulphate and titrating the excess with standard permanganate.

Commercial sodium bismuthate is a brown powder of somewhat indefinite composition ; it may be regarded as NaBiO_3 —a salt of metabismuthic acid, HBiO_3 .

Very small quantities of manganese can be accurately determined by this method which is particularly well adapted for the determination of manganese in steels, ores, rocks, etc. The solution containing the manganese must be free from chloride ; and the oxidation must be carried out in presence of either nitric acid or sulphuric acid.

The following solutions are required :—

Standard Potassium Permanganate Solution.—Dissolve 0.25 gram of the pure salt in cold water and dilute the solution to 250 ml. One ml. corresponds to 0.0003475 gram Mn. (If the permanganate is of doubtful purity, the solution must be standardised.)

Nitric Acid Solutions.—(A) Dilute about 60 ml. of concentrated nitric acid to 250 ml. (B) Dilute 8 ml. of concentrated nitric acid to 250 ml. (The concentrated nitric acid should be colourless, *i.e.* free from oxides of nitrogen.)

Sulphuric Acid Solution (3 per cent.).—Pour 5 ml. of the concentrated acid into water and dilute the solution to 250 ml.

Ferrous Sulphate Solution.—Dissolve 2.25 grams of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 125 ml. of 4N sulphuric acid and dilute the solution to 250 ml. The value of this solution in terms of the standard potassium permanganate solution must be ascertained by carrying out a “blank” determination as follows :—Shake together in a flask 50 ml. of nitric acid (A) with about 1 gram of sodium bismuthate, add 50 ml. of nitric acid (B), and filter through a paper-pulp filter (p. 45).¹ Wash with 50 ml. of nitric acid (B). To the filtrate add 25 ml. of ferrous sulphate solution, and titrate at once with the standard permanganate.

Determination of Manganese in Steel.—Weigh accurately about 1 gram of the steel and transfer it to a 200 ml. conical flask. Add 50 ml. of nitric acid (A) and boil gently until the steel is dissolved and the solution free from oxides of nitrogen.

¹ The paper-pulp filter should be washed with a dilute solution of potassium permanganate containing sulphuric acid and then with water. The same pulp may be used for several successive filtrations. It is better, however, to use an asbestos filter prepared in a similar manner.

Cool, add about 1 gram of sodium bismuthate (in order to oxidise combined carbon), and heat until the pink colour disappears. If manganese dioxide is precipitated, add sufficient sulphurous acid to clear the solution, and then boil for two to three minutes. Cool thoroughly under the tap, or in ice. Add about 2 grams of bismuthate and shake for two minutes. Dilute with 50 ml. of nitric acid (*B*), filter¹ through paper-pulp, and wash with dilute nitric acid (*B*). Add *at once* to the filtrate a measured excess of ferrous sulphate solution (10 ml. to 50 ml. according to the amount of manganese present), and titrate with the standard permanganate without delay.

The percentage of manganese in the sample can then be readily calculated.

Determination of Manganese in Iron Ore.—Take from 0.5 to 2 grams of the ore. Dissolve the weighed portion by warming it in a 200 ml. conical flask (Pyrex glass) with the minimum quantity of concentrated hydrochloric acid—with the addition of a little concentrated nitric acid if organic matter is present. Cool, and add (cautiously) 10 ml. of concentrated sulphuric acid. Manipulate the flask, held in a hand-clamp, over a free flame until all hydrochloric acid is expelled and copious fumes of sulphuric acid are evolved. Allow to cool, dilute with 100 ml. of water, and warm to dissolve the sulphates. Cool, add 2 grams of bismuthate, and shake for at least two minutes. Filter through paper-pulp; rinse the flask and wash the filter with at least 100 ml. of 3 per cent. sulphuric acid. Add to the filtrate (from a weighing-bottle) rather more ferrous ammonium sulphate than is sufficient to decolorise the permanganic acid. Reweigh the bottle and contents to find the amount added. Titrate the excess of ferrous salt with the permanganate. Determine the permanganate equivalent of the ferrous ammonium sulphate.

From the data obtained calculate the percentage of manganese in the ore.

Antimony

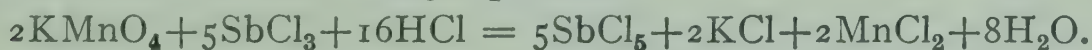
Potassium permanganate oxidises antimonious chloride in presence of hydrochloric acid to antimonie chloride, and

¹ If chromium is present, any delay in filtration may allow oxidation of this to chromate. In the case of high chromium steel, a special method is recommended by Bagshawe (*J. Soc. Chem. Ind.*, 1939, 106T).

antimony in alloys, such as solder, pewter, and type metal, may be determined volumetrically in this way. Tin does not interfere, but if much lead is present, the lead sulphate formed on dissolution of the alloy in sulphuric acid may retain some antimony which escapes oxidation by permanganate. If arsenic is present it must be removed by volatilisation (see p. 180), or a correction made.

Determination of Antimony in Type Metal.—Weigh accurately about 0.5 gram of the alloy (as fine powder or thin foil). Place it in a 150 ml. round-bottomed flask (Pyrex glass if possible), and add 25 ml. of concentrated sulphuric acid. Heat the mixture, gently at first, and then at the boiling-point of the acid until the alloy is completely disintegrated. It is best to manipulate the flask, held in flask tongs or a hand-clamp, over a free flame. Heating is continued until any undissolved lead sulphate is white or nearly so.

Allow the flask to cool, dilute cautiously with water to 100 ml., and allow the lead sulphate to settle out. Decant the clear liquid into a 750 ml. flask, and boil for five minutes to expel sulphur dioxide. Meanwhile, dissolve the lead sulphate by warming with 20 ml. of concentrated hydrochloric acid and 10 ml. of water. Dilute to 100 ml., and boil out sulphur dioxide. Transfer to a 600 ml. flask, diluting during the process with 250 ml. of water, and titrate with decinormal potassium permanganate at room temperature. Cool the main bulk of the antimony solution, add 20 ml. of concentrated hydrochloric acid and 300 ml. of water. Titrate this with the decinormal permanganate without refilling the burette. From the total volume of permanganate used the antimony can be calculated by means of the following equation :—



Persulphates

Persulphates can be determined indirectly by means of standard permanganate, after previous reduction with excess of ferrous sulphate solution :—



The excess of ferrous sulphate and thence that oxidised by the persulphate is then determined by means of N/10 potassium permanganate.

Weigh accurately about 0.4 gram of potassium persulphate into a 500 ml. flask, add 50 ml. of N/10 ferrous sulphate solution from a pipette and 50 ml. of 4N sulphuric acid. Then add 200 ml. of hot water that has been boiled for ten minutes to remove dissolved oxygen. After five minutes, cool the flask to room temperature and titrate the excess of ferrous sulphate with N/10 potassium permanganate.

This method is much more satisfactory for the determination of ammonium persulphate than the acidimetric method described on p 113.

Chromium in Chromium Steel

OUTLINE OF METHOD.—The steel is dissolved in sulphuric acid, the solution oxidised to convert the chromium to chromate, and this is estimated by the addition of standard ferrous salt solution followed by a back-titration with potassium permanganate.

Dissolve 2 grams of the sample in 10 ml. of concentrated sulphuric acid and 60 ml. of water in a 600 ml. conical beaker, oxidise by adding 1 ml. of concentrated nitric acid, and boil for five minutes. Dilute to 250 ml. with hot water, bring to the boiling-point, and add carefully a 2.5 per cent. solution of potassium permanganate until a very faint permanent precipitate is formed. Add 10 drops of the permanganate solution in excess, and boil for ten minutes. Add a crystal or two of manganous sulphate, and again boil for ten minutes. Cool, and filter through an asbestos pad, washing well with water.

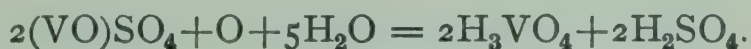
Run in from a burette an excess of decinormal ferrous ammonium sulphate, and titrate back with decinormal potassium permanganate solution until a faint pink colour is obtained. The difference between the ferrous ammonium sulphate solution run in, and that remaining in excess, is equivalent to the chromate formed. From the fact that 6FeSO_4 is equivalent to $\text{K}_2\text{Cr}_2\text{O}_7$ (p. 132), calculate the percentage of chromium in the chromium steel.

The titre of a ferrous ammonium sulphate solution changes with time, and must be checked each day the solution is used.

For steels containing less than 0.25 per cent. of chromium, add three or four crystals of potassium permanganate during the dissolution of the sample. For samples containing more than 10 per cent. chromium, make up the solution to a known volume after filtration and take a suitable fraction for titration.

Vanadium

Vanadium in the form of vanadate can be conveniently determined by reduction of the solution with sulphur dioxide. After removal of the excess of sulphur dioxide, the vanadyl salt present is reoxidised to vanadate by standard potassium permanganate.



Exercise.—Weigh out accurately about 1 gram of ammonium vanadate, dissolve it in about 75 ml. of hot water, and after cooling make up the solution to 100 ml. Measure out 25 ml. into a conical flask, add 50 ml. of water, and 25 ml. of dilute sulphuric acid. Heat to boiling, and pass sulphur dioxide for two minutes after the colour of the solution has become clear blue. Boil off the excess sulphur dioxide, hastening the operation by passing carbon dioxide through the liquid. Cool to 70°, and titrate with decinormal potassium permanganate until a pink tinge persists for thirty seconds.

- If the sample of vanadate contains iron, ferrous sulphate will be present in the reduced liquid, and this must first be carefully oxidised, testing for its disappearance by ferricyanide as external indicator.

STANDARD POTASSIUM DICHROMATE

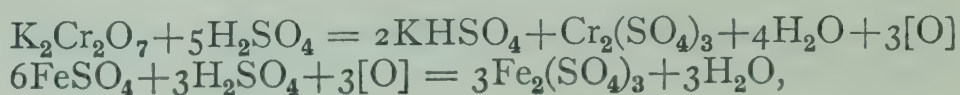
(*N/10 solution contains 4.903 grams $\text{K}_2\text{Cr}_2\text{O}_7$ per litre*)

Dichromate, unlike permanganate, is unaffected by moderate quantities of hydrochloric acid, and it is therefore suitable for the titration of iron when stannous chloride has been used as reducing agent. The solution is quite stable.

As it is not possible to detect a slight excess of potassium dichromate by any change in colour, the end-point of the reaction must be determined by means of (a) potassium ferricyanide, which is used as an external indicator, or (b) an indicator such as diphenylamine, which is added to the solution being titrated. The dichromate must be standardised with the same indicator as that which is subsequently to be used.

Weigh accurately about 4.9 grams of pure potassium dichromate. Transfer to a standard litre flask, dissolve in water, and dilute the solution to 1 litre.

The interaction between potassium dichromate and ferrous sulphate in presence of acid is as follows :—



or, combining these equations,



The molar weight of the dichromate thus provides 48 grams (six gram-equivalents) of available oxygen, and a decinormal solution therefore contains one-sixtieth of the molar weight per litre. If the solution is prepared from pure potassium dichromate, the concentration should correspond exactly to the weight of the salt taken. Standard potassium dichromate is used chiefly for the determination of iron, and 1 litre of a decinormal solution will oxidise 5.585 grams.

Titration with Dichromate using Ferricyanide as Indicator.

—The solution to be titrated should be placed in a beaker (or conical flask if preferred) and must contain considerable sulphuric or hydrochloric acid; add, therefore, about 50 ml. of dilute acid, unless the solution is known to contain a corresponding quantity, and then run in the dichromate solution from a burette until all the iron is oxidised.

The potassium ferricyanide solution must be freshly prepared and very dilute (about 0.2 per cent.), and it must contain no ferrocyanide. To prepare it, take a crystal of potassium ferricyanide weighing slightly more than 0.5 gram, rinse it several times with small quantities of cold water (in order to remove superficial ferrocyanide), and dissolve it in 25 ml. of water. Dilute 5 ml. of this solution to 50 ml. The solution decomposes somewhat rapidly, and a fresh one must be made from the solid for each set of titrations.¹

The titration is carried out as follows :—Using a small pipette make a series of single drops of ferricyanide solution on a *dry* white tile. Tiles with twelve or more depressions in the surface are convenient for this purpose. Run in the dichromate solution slowly from a burette while swirling the ferrous solution, and from time to time remove a drop of the

¹ After a little experience it is easy to prepare a solution of a suitable concentration by carefully rinsing a very small crystal of ferricyanide and dissolving it in a test-tube of water.

titrated solution by means of a rod. Add this drop to one of the ferricyanide drops on the white tile, and observe whether a blue colour is produced, which will be the case if any ferrous salt is still present. The rod *must always* be washed before it is returned to the solution being titrated.

When the ferrous iron content of the solution is not known even approximately, time may usually be saved by making a rough titration first, adding the dichromate solution two or more millilitres at a time between each test with ferricyanide solution. A second titration is then carried out without testing with ferricyanide until an amount of potassium dichromate, known from the first titration to be slightly insufficient, has been run in. The end-point is then approached by small additions of dichromate, finally adding single drops.

While the solution still contains an appreciable amount of ferrous salt, a blue coloration is obtained at once with ferricyanide; but as the amount of ferrous salt diminishes, the blue coloration becomes less apparent, until only a faint blue-green tint is seen. It is only when finally no trace of this develops that no ferrous salt remains and the titration is finished.

Since the blue-green tint develops somewhat slowly near the end it is advisable to allow the test drops on the tile to stand about five minutes before deciding whether the ferrous salt has all been oxidised. Delay on this account can be avoided by proceeding with the titration and writing down the burette readings corresponding to the ferricyanide tests carried out in a definite order on the tile. The required burette reading will of course be that corresponding to the first drop test which shows no blue-green tint after standing five minutes. In this way the end-point can be obtained to one drop or less of dichromate.

In the second titration described above, the error introduced by removing drops of the solution will be very small, because most of the ferrous salt is oxidised before the first drop is removed. The error may be still further reduced by making a third titration in which the end-point can be approached within 0.25 ml. before testing with the ferricyanide solution.

If the ferricyanide solution contains ferrocyanide, it is impossible to obtain a sharp end-point, since ferric salts give a blue colour with ferrocyanide. For this reason also the ferricyanide must not be exposed to direct sunlight.

Titration with Dichromate using Diphenylamine as

Indicator.—The use of diphenylamine enables rapid titrations of ferrous solutions to be carried out with potassium dichromate in the presence of chlorides and other substances which react with potassium permanganate.

When treated with various oxidising reagents (*e.g.* nitrates, traces of which may thus be detected), diphenylamine gives a very intense blue colour from oxidation products, the full depth of which does not in all cases develop immediately.

The concentration of hydrochloric or sulphuric acid in the ferrous solution should be about normal, but may be between 0.5 and 2N. Shortly before the end-point a blue-green colour will develop because of the high ratio of ferric to ferrous iron in the solution, as ferric iron has a slight oxidising action on diphenylamine. The addition of a phosphate or fluoride diminishes this effect by the formation of a complex which reduces the oxidising tendency of the solution, and has itself less colour than ferric iron. This point is more fully dealt with on p. 135.

In those cases in which stannous chloride has been used to reduce ferric salts to ferrous (p. 143), the excess of mercuric chloride subsequently added should be kept as small as possible, as this reagent retards the development of the colour. A solution of sodium diphenylamine sulphonate is more satisfactory than diphenylamine if mercuric chloride is present (see p. 137).

Under certain conditions the colour change is reversible, and it is possible to titrate an acid solution of dichromate to which diphenylamine has been added, by means of a ferrous salt.

Standardisation of Potassium Dichromate without using an Indicator

To 25 ml. of the potassium dichromate solution, add 50 ml. of an approximately decinormal solution of ferrous ammonium sulphate in at least 2N sulphuric acid. Titrate the excess of ferrous salt with standard permanganate, taking as the end-point the grey colour produced by the smallest excess of permanganate in conjunction with the green chromic salt. A further 25 ml. of ferrous ammonium sulphate solution is then titrated with the permanganate. The volume of permanganate equivalent to 25 ml. of the dichromate solution can thus be determined.

ANALYSES INVOLVING THE USE OF STANDARD PERMANGANATE OR DICHROMATE SOLUTIONS

Titration with Permanganate in Presence of Hydrochloric Acid.—The determination of iron by volumetric methods may be made with either a standard permanganate or a standard dichromate solution. If the ferrous salt solution contains no hydrochloric acid, there is little to choose between the two methods in point of accuracy, but the permanganate titration is certainly the more convenient. If the solution contains hydrochloric acid or any chloride, it cannot be accurately titrated with permanganate unless precautions are taken, because the hydrochloric acid (even when cold and dilute) is oxidised by permanganate in presence of a ferrous salt, and a serious error results. Another source of error is that the end-point of the titration is unsatisfactory on account of the yellow colour of the ferric chloride that is formed.

It is better to avoid a permanganate titration if the ferrous salt solution contains hydrochloric acid, although it is possible to overcome the difficulty almost entirely by adding about 2 grams of hydrated manganese sulphate and 3 ml. of syrupy phosphoric acid. The mixture is then titrated *very slowly* with the permanganate at room temperature. If any brown or yellow colour is noticed, insufficient phosphoric acid has been added and the titration will be inaccurate. The addition of manganese sulphate lowers the oxidation potential of the potassium permanganate, and the phosphoric acid forms a complex with the ferric ions, and thereby decreases the oxidation potential of the ferrous ions which depends on the ratio of the concentration of the ferrous to that of the ferric ions (see p. 218).

Iron in Iron Wire

Commercial iron is not chemically pure, although the amount of impurity in some varieties of iron is very small. As determined by volumetric methods, commercial iron sometimes appears to contain more than 100 per cent. of pure iron. This arises from the presence of impurities (carbides, etc.) that have a greater reducing action when dissolved in acid than has an equal weight of pure iron.

The determination of the "apparent" percentage of iron in iron wire is made as follows:—Remove any trace of rust from some fine-drawn, soft iron wire ("flower wire") by means of emery cloth, and then clean the wire with filter paper. Weigh accurately about 1.4 gram of the wire and place it in a 400 ml. flask fitted with a rubber stopper carrying a straight tube of narrow bore (5 mm.) about 50 cm. long. Add 100 ml. of 4N sulphuric acid, and warm the flask gently, preferably on a water-bath, until all the iron has dissolved, and only small particles of carbon remain. Then cool rapidly by gentle rotation in cold water, and make up to 250 ml. in a standard flask, using recently boiled and cooled distilled water. Allow the suspended particles of carbon to settle, and titrate 25 ml. portions of the solution with standard permanganate or dichromate. If permanganate is used, the end-point has been reached when the pink colour persists throughout the solution for a few seconds.

Calculate the percentage of iron in the wire, assuming that ferrous sulphate is the only reductant present.

Iron in Ferrous and Ferric Compounds

If the iron is wholly present in the ferrous condition, it is determined by direct titration with standard permanganate or dichromate.

If the iron is present, wholly or partly, as ferric salt, it must be reduced to the ferrous state before titration. The common methods of reduction are:—

- (1) With zinc and acid (this method can not be used in conjunction with dichromate if potassium ferricyanide is used as external indicator).
- (2) With sulphur dioxide.
- (3) With hydrogen sulphide.
- (4) With stannous chloride.
- (5) With the silver reductor.

As the reducing agents themselves also reduce permanganate or dichromate solutions, any excess of the reducing agent must be removed before the titration. If the solution is to be titrated with standard permanganate in the presence of hydrochloric acid or a chloride, phosphoric acid and manganese sulphate must be added (see p. 135).

If titanium is present with the iron it is advisable to use either sulphur dioxide or hydrogen sulphide or the silver reductor, as these do not reduce titanous salts.

Exercise.—Determine the percentage of iron in iron alum [ferric ammonium sulphate, $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$], using the various methods of reduction described below, and compare the results.

Dissolve about 24 grams (weighed to the nearest centigram) of powdered iron alum in water to which 50 ml. of 4N sulphuric acid have been added. Dilute in a standard flask to 500 ml. and use 25 ml. for each determination.

Reduction with Zinc.—To 25 ml. of the iron alum solution contained in a conical flask, add 25 ml. of water, 10 ml. of concentrated sulphuric acid and 10 grams of “pure,” granulated zinc. Two or three drops of copper sulphate solution may be added to hasten the dissolution of the zinc. Warm *gently* and allow the reaction to continue until the solution appears quite colourless, and then test for ferric salt :—Place a drop of potassium thiocyanate solution on a white porcelain surface, such as a crucible lid, and then bring into contact with the drop a *trace* of the iron solution which has been withdrawn from the flask by means of a *thin* glass rod or a capillary tube ; a red coloration indicates that reduction has not gone far enough, and this must be continued until the test only produces a faint tinge.

After reduction wait until *almost* the whole of the zinc has disappeared, additional sulphuric acid being added, if necessary, to effect this. (An insoluble residue, chiefly lead, nearly always remains.) Filter through a small plug of glass-wool into a flask containing 25 ml. of dilute sulphuric acid. Rinse the original flask and any undissolved residue several times with dilute sulphuric acid, pouring this also through the filter, and wash the latter carefully with water. Titrate the solution with standard permanganate.

Since the best commercial zinc invariably contains at least a trace of iron, a “blank” determination must be carried out in order to find the correction for that impurity. In the “blank” determination the same quantities of zinc and sulphuric acid are used but the ferric salt is omitted, and, after the zinc has *almost* completely disappeared, the solution is filtered and titrated with the permanganate. With good

zinc, only a few drops of permanganate should be required in the "blank," and an equal amount must be deducted from the volume of permanganate required for the titration of the reduced ferric salt solution.

Reduction with Zinc in a Jones "Reductor."—The reduction of a ferric salt with zinc may be more rapidly accomplished by using a Jones "reductor" (Fig. 35), in which a large surface of zinc is exposed to the solution. The part A to B of the reductor is about 25 cm. long and 2 cm. wide, and is filled with amalgamated zinc granules. The cup C is about 8 cm. long and 4 cm. wide. A tap is provided at T. The reductor is held in a clamp and is fitted into a 400 ml. filter-flask which rests on a block of wood. If the block is removed, the flask can be removed without disturbing the rest of the apparatus.

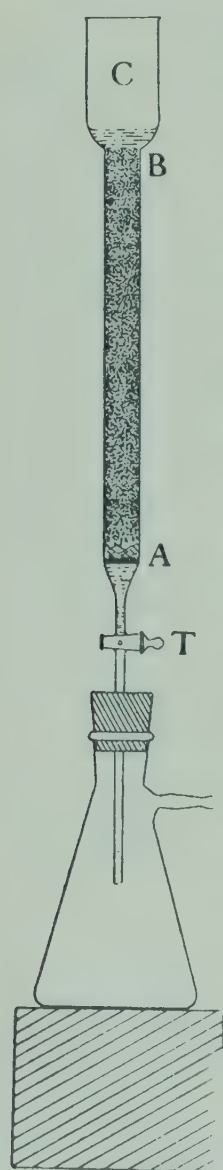


FIG. 35.

The amalgamated zinc is prepared as follows:— In a large beaker or basin place 250 grams of zinc granules (sieved through a 10- or 20-mesh screen) and cover them with normal hydrochloric acid, stir for a moment, and then add 150 ml. of mercuric chloride solution (0.2N). Stir vigorously until hydrogen ceases to be evolved (about two minutes). Decant the solution and wash the zinc thoroughly by decantation with distilled water. After draining the water as completely as possible, dry the zinc on a clock-glass in the air-oven.

Place a perforated porcelain disc in the tube at A, and cover this with about 0.3 gram of glass-wool. Then pour into the tube about 30 milligrams of Gooch crucible asbestos mixed with water and drain the water by gentle suction.

Prepare approximately 0.2N sulphuric acid by diluting 50 ml. of the dilute acid to 500 ml. Fill the reductor column from A to B with this acid and add the amalgamated zinc in small portions until the tube is filled from A to B with the zinc. It will be necessary to drain off some of the sulphuric acid, but the level of the acid must never be allowed to fall below the level of the zinc. Run about 200 ml. of the acid, followed by 100 ml. of water, through the reductor, using gentle suction, keeping the column filled with liquid so that

no air can enter. [This precaution must always be observed in using the reductor, which should be corked when not in use.] Empty and rinse the filter-flask. The apparatus is now ready for use.

“Blank” determination.—Since the zinc is seldom entirely free from iron, a “blank” determination must be made as follows:—Run 100 ml. of 0.2N sulphuric acid, followed by 100 ml. of water, through the reductor, taking care to close the tap T before the surface of the zinc is exposed to the air. Detach the flask, add 10 ml. of 4N sulphuric acid, and titrate with standard permanganate. With good zinc only 1 to 2 drops (less than 0.1 ml.) of decinormal permanganate should be required. Repeat the determination to make sure that the “blank” titration is constant.

Reduction of the ferric salt solution.—Measure 25 ml. of the iron alum solution into a small beaker and add an equal volume of water. (The concentration of acid in this solution is about 0.2N.) Pour the solution into the cup of the reductor, open the tap, and regulate the suction so that about two minutes are required for the 50 ml. of solution to pass through the column. Close the tap before the zinc is exposed. Rinse the beaker with 50 ml. of 0.2N acid and run this also through the reductor. Finally, rinse the beaker and the cup C with water—using 100 ml. in all—this water also being drawn through the zinc column. Close the tap before the cup is quite empty. Remove the filter-flask, add 10 ml. of 4N sulphuric acid, and titrate the solution with standard permanganate. Deduct the correction indicated in the “blank” determination.

Reduction with Silver in a Jones “Reductor.”—A reductor has been described by G. H. Walden, L. P. Hammett, and S. M. Edmonds (*J. Amer. Chem. Soc.*, 1934, **56**, 350), in which silver is used in place of amalgamated zinc, and the ferrous salt produced is titrated with standard ceric sulphate. Instead of ceric sulphate, J. L. Henry and R. W. Gelbach (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 49) suggest the use of potassium dichromate for the titration. The advantage of using silver instead of zinc lies in the fact that silver is easily prepared free from iron, while zinc is nearly always contaminated with it. Silver, however, will only partially reduce ferric sulphate in the presence of dilute sulphuric acid, but in the presence of normal hydrochloric acid reduction is virtually complete, since when

metallic silver is in contact with the very sparingly soluble silver chloride the redox potential of the system is about 0.22 volt, whereas that of the ferric-ferrous system is 0.70 volt in N hydrochloric acid. The ferric ion is therefore almost completely reduced, and when normal hydrochloric acid is used, titanous, chromous, and manganous salts do not interfere. The ferrous solution is titrated with potassium dichromate using either potassium ferricyanide or diphenylamine as indicator.

The method is particularly suitable for use in rock analysis, provided proper precautions are taken.

Prepare the silver by dissolving in a 600 ml. beaker about 35 grams of silver nitrate in 400 ml. of distilled water to which about 5 ml. of dilute nitric acid have been added. Put in about 10 grams of electrolytic copper foil, and stir the mixture mechanically until a few drops of the clear solution give no immediate turbidity with dilute hydrochloric acid. Pour the solution and precipitated silver through a funnel into another 600 ml. beaker so that the excess of copper foil is retained by the funnel. Wash the silver three times by decantation with approximately normal sulphuric acid and transfer it to a Jones Reductor of the same size as that described on p. 138. Continue the washing with N sulphuric acid until no reaction for copper is given with potassium ferrocyanide in the liquid passing through the column, which must always have enough liquid in it to cover the silver.

Measure 25 ml. of the iron alum solution into a small beaker and add 2.5 ml. of concentrated hydrochloric acid. Prepare a solution of approximately normal hydrochloric acid by diluting 27 ml. of the concentrated acid to 300 ml. Place about 0.5 gram of sodium bicarbonate in the receiving flask (to provide an atmosphere of carbon dioxide to prevent aerial oxidation of the ferrous iron) and pour the iron solution down a small glass rod into the cup of the reductor. Open the tap of the reductor and allow the solution to percolate through the column at a rate not greater than 20 ml. per minute. It will probably not be necessary to use suction. Wash the column with six lots of the prepared hydrochloric acid, using about 150 ml. in all, first pouring each lot into the small beaker to wash it thoroughly and allowing each to run down to the level of the silver before adding the next. Titrate the ferrous solution with standard potassium dichromate using potassium ferricyanide as external

indicator ; or add 5 ml. of syrupy phosphoric acid, and two drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid, and run in the potassium dichromate until the colour changes from green to violet blue.

For a discussion of the errors associated with the silver reductor, especially in rock analysis, see Miller, C. C., and Chalmers, R. A., *Analyst*, 1952, **77**, 2.

Reduction with Zinc Amalgam.—This is a convenient form in which to use zinc as a reducing agent, and reduction can be effected very rapidly.

The amalgam is prepared by heating 3 to 4 grams of zinc ("free from arsenic") with 100 grams of mercury and about 20 ml. of dilute sulphuric acid for about an hour in a conical flask on a water-bath. The amalgam is then washed by shaking with water, and filtered through glass-wool from any undissolved zinc. It can be used repeatedly, as very little zinc is wasted, hydrogen not being generated in appreciable quantities.

To reduce a solution of ferric alum by means of zinc amalgam, pour 100 grams of the amalgam into a stoppered bottle of about 150 ml. capacity. Add 25 ml. of the decinormal iron alum solution, and 25 ml. of 4N sulphuric acid. Insert the stopper, and shake vigorously for about one minute, when the reduction will be complete. Pour off the colourless solution into a flask, taking care not to allow any of the amalgam to pass over. This is more certainly effected by pouring the reduced solution through a No. 3 sintered glass crucible (p. 238). In carrying out this process, wash the stopper and mouth of the bottle by means of a wash-bottle. Add to the amalgam about 25 ml. of 4N sulphuric acid, insert the stopper and shake. Pour off as before, and repeat the process. This dilute acid is used instead of water for washing, since water gives a turbid liquid which has a slight reducing effect on permanganate.

Titrate the reduced solution in the filter-flask with decinormal permanganate, taking as the end-point the first production of a pink tinge throughout the liquid, though this fades fairly rapidly.

Alternative Method for Reduction with Zinc Amalgam.—The following method, by G. F. Smith and L. T. Kurtz [*Ind. Eng. Chem., Anal. Ed.*, 1942, **14**, 854], has the advantage that the titration of the ferrous salt is carried out in the vessel in which it is reduced, thereby avoiding the troublesome

process of washing the bottle in which the reduction was effected with the rather concentrated sulphuric acid. Also a more stable end-point is obtained than in the other method, but a mechanical stirrer is necessary.

A wide-mouthed stoppered bottle of about 175 ml. capacity is suitable for use with the same quantities of solutions as specified above. The reduction is carried out as above, but instead of pouring off the reduced solution, the stopper is removed and washed along with the sides of the bottle, and about 40 ml. of carbon tetrachloride are added. This forms a layer over the amalgam and isolates it from the iron solution layer above. An electric stirrer is inserted in the iron solution, and the titration carried out, care being taken to avoid breaking the carbon tetrachloride layer. When a pink colour is permanent for half a minute this is taken as the end-point. The carbon tetrachloride can be separated by means of a separating funnel, and used for another titration.

Reduction with Sulphur Dioxide.—If the solution is acid, it must be made nearly neutral by adding ammonia until a slight permanent precipitate of ferric hydroxide forms. The reducing agent is then added, either in the form of sulphurous acid solution or a sulphite, or by passing a current of sulphur dioxide from a siphon of the liquefied gas through the cold solution. The solution after the reducing agent is added, must be *slightly acid* to litmus; if it is alkaline, or strongly acid, no reduction takes place. The excess of sulphur dioxide is removed by adding acid and passing a current of carbon dioxide through the boiling solution.

Measure 25 ml. of the iron alum solution into a conical flask fitted with a cork carrying two glass tubes, one reaching almost to the bottom of the flask, and the other just through the lower end of the cork. Add ammonia until a very slight permanent precipitate forms, and then 25 ml. of freshly prepared sulphurous acid solution. Boil the mixture gently until the issuing steam is free from sulphur dioxide. (Test with potassium dichromate solution on filter paper after 15 minutes.) Pass a fairly rapid current of carbon dioxide through the flask while cooling it in a basin of water. Rinse the gas delivery tube and remove it. Add about 20 ml. of dilute sulphuric acid, and titrate the solution with standard permanganate or dichromate.

Reduction with Hydrogen Sulphide.—If a current of

hydrogen sulphide is passed through a solution of a ferric salt, sulphur is precipitated and the ferric salt is almost completely reduced to the ferrous state. The solution should contain about 2 per cent. by volume of concentrated sulphuric acid. The excess of hydrogen sulphide is removed by passing a current of carbon dioxide through the boiling solution.

Add 10 ml. of dilute sulphuric acid to 25 ml. of the iron alum solution contained in a 200 ml. flask. Dilute to about 50 ml., pass hydrogen sulphide into the cold solution for at least fifteen minutes, then heat until boiling, and continue the current of gas until the precipitated sulphur has coagulated. Allow the solution to cool somewhat without interrupting the gas current, and then filter into another flask, rinsing the original flask and washing the filter carefully. Dilute the solution, if necessary, to about 100 ml., and pass a fairly rapid current of carbon dioxide through the boiling solution until hydrogen sulphide cannot be detected in the escaping gas by means of lead acetate paper.¹ Cool the solution—without interrupting the gas current—and titrate it with standard permanganate or dichromate.

The acidity of a ferric solution which is to be reduced by hydrogen sulphide should be between 0.4N and 0.5N. Phosphoric acid must not be present.

Unless the conditions are carefully controlled, the method is likely to give high results because of the formation of stable, oxidisable sulphur compounds during the reduction process (Lundell, G. E. F., and Knowles, H. B., *J. Amer. Chem. Soc.*, 1921, 43, 1560). The method is subject to interference by vanadium, which is also reduced.

Reduction with Stannous Chloride.—Stannous chloride is added to the ferric salt solution containing hydrochloric acid until the colour is discharged. The excess of the stannous chloride is destroyed by adding mercuric chloride, and the solution is then titrated with standard dichromate.

The stannous chloride solution may be prepared by dissolving 3 grams of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml. of concentrated hydrochloric acid, and diluting to about 100 ml.²

¹ Ten minutes is usually sufficient. If the solution is milky (on account of sulphur in suspension) a minute trace of hydrogen sulphide, which may be neglected, will always be found in the escaping gas.

² The side-shelf reagent is suitable, if it has been recently prepared.

To 25 ml. of the iron alum solution (p. 137) contained in a 300 ml. flask, add 5 ml. of concentrated hydrochloric acid, heat until boiling, and then run in the stannous chloride drop by drop from a burette until the yellow colour of the solution is just discharged. A slight excess (one or two drops) of the stannous chloride is essential, but a large excess must be carefully avoided. *Cool the solution* in the flask,¹ dilute to 150 ml., and add (rapidly, and with stirring) about 10 ml.² of saturated mercuric chloride solution. A very slight, *white* precipitate should form. If no precipitate appears, insufficient stannous chloride has been added, whilst a grey or black precipitate shows that too much stannous chloride was used, and the metallic mercury liberated will interfere with the subsequent titration. In either case the experiment must be rejected.

Titrate the turbid mixture with standard dichromate, or add phosphoric acid (see p. 135) and titrate with permanganate. If standard potassium dichromate is used, either potassium ferricyanide may be used as an external indicator, or a solution of sodium diphenylamine sulphonate as internal indicator, this indicator being less affected by excess of mercuric chloride than is diphenylamine.

Sodium diphenylamine sulphonate is prepared by stirring 0.32 gram of barium diphenylamine sulphonate into 90 ml. of water, and adding 0.5 gram of sodium sulphate in 10 ml. of water. After the mixture has been stirred for some time, the precipitate is filtered off. Six to eight drops of the filtrate are used for each titration, 25 ml. of a mixture of sulphuric and phosphoric acids (p. 149) being added to remove the ferric ions as they are formed. The end-point is shown by a change from the green colour of the chromic ion to a bluish grey.

Total Iron in a Mineral

(Hæmatite ; Magnetite ; Bog Iron Ore ; etc.)

If the ore is in large pieces, a representative sample is crushed (without grinding) in a clean, steel percussion mortar. The coarse powder is then finely ground in an agate mortar.

¹ This may be done conveniently by covering the mouth of the flask by a small inverted beaker, and placing under the tap.

² If diphenylamine is to be used as an indicator, not more than 3 ml. of mercuric chloride must be added.

Iron ores sometimes dissolve very slowly in acid unless they are reduced to an impalpable powder.

Dissolving the Ore.—Weigh accurately about 1 gram of the ore, or a larger quantity if the ore contains but little iron. If the ore contains carbonaceous matter (as is often the case), weigh it in a porcelain crucible, and heat it to dull redness for ten minutes.

Transfer the weighed portion of the ore, after ignition, to a 200 ml. flask, and add 15 ml. of concentrated hydrochloric acid. Warm on the steam-bath for some time, and then keep near the boiling-point of the acid until the undissolved residue, if any, is perfectly white. (Nothing is gained by boiling vigorously—this merely reduces the concentration of the acid.)

If after half an hour the residue is still coloured, add to the hot liquid at intervals 1 to 2 ml. of stannous chloride (avoiding excess); rapid dissolution usually follows in the case of a hæmatite ore. If excess of stannous chloride is inadvertently added, add potassium permanganate until the yellow colour of the ferric iron returns.

When as much as possible of the ore has been brought into solution, and whether the residue is coloured or not, dilute with a little water, and filter into a 100 ml. standard flask. Rinse the original flask and wash the filter carefully, first with dilute hydrochloric acid and then with water, using as little as possible. If the filtrate contains all the iron, cool and make it up to 100 ml.

If the insoluble residue is coloured, and therefore probably contains iron (provided organic matter was destroyed by ignition), incinerate the filter paper together with the residue in a porcelain crucible (p. 243). Then add 2 to 3 grams of previously fused potassium hydrogen sulphate (pyrosulphate), heat cautiously, and keep the mixture fused until the dark specks of iron oxide have disappeared. Cool, place the crucible in a small porcelain basin, and dissolve the solid residue in the minimum quantity of dilute sulphuric acid. Filter if necessary (most of the silica remains undissolved), and receive the filtrate and rinsings in the flask containing the main solution of the ore. Dilute to 100 ml.

Titration of the Solution.—Use 25 ml. of the solution for each titration. If stannous chloride was used in the preparation of the solution, the reduction of the ferric salt must also be

effected with stannous chloride; otherwise hydrogen sulphide or sulphur dioxide may be used as the reducing agent. After reduction, the solution may be titrated with either standard dichromate or permanganate. If standard permanganate is to be used, phosphoric acid and manganese sulphate must be added before the titration (p. 135).

Methods for Refractory Oxides and Silicates.—The acid treatment described above will not always dissolve all the iron in the sample. The addition, from time to time, of a few crystals of potassium chlorate to the concentrated hydrochloric acid promotes the dissolution of a refractory oxide such as magnetite. The same treatment also serves to oxidise any sulphides or carbonaceous matter the sample may contain. If potassium chlorate has been added, the solution should then be boiled for some time, or evaporated to a small volume, in order to free it from chlorine.

Natural silicates and artificial siliceous slags must be decomposed, as a rule, by fusing with sodium carbonate, or “fusion mixture,” as described under silica (p. 386). If only the iron in the silicate is to be determined, it is not necessary to evaporate to dryness in order to remove the silica. The acid solution obtained after the fusion is treated as follows:—Warm the solution in a beaker, add a little bromine water and heat until boiling, in order to oxidise any ferrous salt. Precipitate the iron (together with aluminium, manganese, etc.) by adding ammonia in slight excess. Boil for a minute, allow the precipitate to settle, filter, transfer the precipitate to the filter, and wash it thoroughly with hot water. Place the funnel in a flask, and dissolve the precipitate on the filter by pouring through the funnel a hot mixture of 10 ml. of concentrated hydrochloric acid and 10 ml. of water. Wash the filter carefully, at first with hot dilute hydrochloric acid and then with hot water. Reduce with stannous chloride, and titrate with standard potassium dichromate (p. 143).

Silicate rocks may also be decomposed by treatment with hydrofluoric and sulphuric acids. A platinum crucible must be used. Decomposition is effected by heating the mixture on a steam-bath. The hydrofluoric acid is then evaporated off, either on the steam-bath or by *cautious* heating on the radiator described on p. 37. The sulphuric acid is then removed by heating on the radiator, and the sulphates left are fused with

potassium pyrosulphate. This fusion introduces platinum into the analysis, which precludes the use of the stannous chloride method (in which platinum interferes). The cooled pyrosulphate melt is dissolved in normal hydrochloric acid, and the silver reductor is used to reduce the iron (see footnote p. 445).

Separate Determination of Ferrous and Ferric Iron in a Mineral

Ferrous Iron.—The exact determination of ferrous iron in minerals is a very difficult operation. Reference may be made to Hillebrand's *Analysis of Silicate and Carbonate Rocks* for a description of the methods employed and the difficulties encountered.

Certain precautions are necessary during the grinding, as it is found that considerable oxidation may occur if the sample is ground to a fine powder in the ordinary manner. A very fine powder is usually essential, and oxidation may be prevented by grinding *the weighed sample* under alcohol in an agate mortar. The ground product must then be transferred through a funnel to a flask using a jet of alcohol and assisting the process with a rubber-tipped rod. The alcohol is then removed by distillation on a water-bath, a current of carbon dioxide being passed through the flask towards the end of the distillation.

Dissolution must then be effected in absence of air. If the mineral dissolves in hydrochloric acid, the operation may be conducted in the flask which has been filled with carbon dioxide, and which is kept filled by passing a current of carbon dioxide into the flask until solution is complete. The solution is then cooled in an atmosphere of carbon dioxide, diluted if necessary, and titrated with standard potassium dichromate.

If the mineral does not dissolve readily in hydrochloric acid, it must be decomposed in absence of air by means of hydrofluoric acid in presence of sulphuric acid. (For details, see Hillebrand, *loc. cit.*)

Ferric Iron.—The total iron is then determined by one of the methods already described, and the difference between the total iron and the ferrous iron gives the amount present in the ferric state.

Iron and Chromium in Chrome Iron Ore

Decomposition of the Ore.—Grind the ore *very finely* in an agate mortar. Weigh accurately about 0.5 gram, transfer to a nickel crucible, and mix thoroughly by means of a thin glass rod with 5 to 6 grams of sodium peroxide. Heat the crucible gently with a very small Bunsen flame until the contents melt, and then keep the mixture at dull red heat for about ten minutes. Remove the flame until a crust forms, then add another gram of sodium peroxide, and heat again to dull redness for about five minutes.

Place the crucible, after cooling, in a porcelain basin, add about 50 ml. of water, and warm until the yellow mass has dissolved. Remove the crucible and rinse it. If the solution is purple in colour, add a little more sodium peroxide, and then boil the solution in the covered basin until the excess of sodium peroxide is *completely* decomposed. In order to destroy the large excess of sodium hydroxide in the solution, add about 5 grams of ammonium carbonate and boil again. Filter off and wash the precipitate thoroughly. Determine the iron in the precipitate and the chromium in the filtrate.

Iron.—Dissolve the precipitate by pouring hot hydrochloric acid (equal volumes of concentrated acid and water) into the filter, and receive the solution in a 300 ml. conical flask. Wash the filter with hot dilute hydrochloric acid and then with hot water. (If any dark-coloured residue remains, it must be fused again with sodium peroxide.) Reduce the ferric salt in the solution with stannous chloride, and titrate with standard dichromate (p. 143).

Chromium.—Add 4N sulphuric acid to the filtrate until it is acid (orange-yellow), and then add 25 ml. more acid. Allow the solution to cool; then reduce the dichromate by adding a known excess of ferrous ammonium sulphate, as follows:—Place several grams of the powdered ferrous salt in a weighing-bottle and weigh the bottle and contents; then add the salt to the chromate solution gradually, while swirling, until it is free from orange-yellow colour, and until a small drop of the solution gives a blue coloration with a drop of freshly prepared potassium ferricyanide solution.

Titrate the excess of ferrous salt in the solution with standard dichromate. Also weigh the weighing-bottle again, and thus determine the weight of ferrous ammonium sulphate used.

Determine the purity of the ferrous ammonium sulphate by titrating a known weight of it with the standard dichromate.

Chlorate

The following method, described by A. J. Boyle, V. V. Hughey, and C. C. Casto (*Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 370), depends on the reduction of the chlorate ion to the chloride ion by the addition of excess of ferrous ammonium sulphate in the presence of hydrochloric acid with ammonium molybdate added to act as a catalyst. The excess of ferrous ammonium sulphate is titrated with potassium dichromate solution using diphenylamine sulphonate as indicator. The following solutions are required :—

(1) *Ferrous Ammonium Sulphate*.—About 0.25N. Dissolve 10 grams of the pure salt in 100 ml. of dilute sulphuric acid.

(2) *Ammonium Molybdate*.—Prepare a 10 per cent. solution.

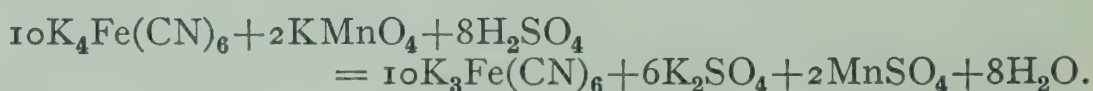
(3) *Sulphuric-phosphoric Acid Mixture*.—Add 10 ml. of each acid to 50 ml. of water and dilute to 100 ml.

Procedure.—Weigh out accurately about 0.2 gram of potassium chlorate, dissolve it in a little water, and make up to 100 ml. in a standard flask. To 10 ml. of this solution contained in a 500 ml. flask add 10 ml. of the ferrous ammonium sulphate solution, 3 drops of the ammonium molybdate, and 40 ml. of concentrated hydrochloric acid. Allow to stand for one minute to ensure completion of the reaction. Add 20 ml. of the sulphuric-phosphoric acid mixture and dilute with distilled water to about 200 ml. Add 3 drops of diphenylamine indicator, and titrate with standard potassium dichromate solution to a purple end-point. Keep the liquid as a colour standard for the next titration.

Repeat the titration, substituting 10 ml. of distilled water for the 10 ml. of the chlorate solution. The difference between the two titres gives the volume of standard dichromate solution equivalent to 10 ml. of the solution of potassium chlorate. Since $\text{KClO}_3 = 3\text{O} = 6\text{FeSO}_4 = \text{K}_2\text{Cr}_2\text{O}_7$, 1 litre of normal potassium dichromate solution is equivalent to 4.25 grams of potassium chlorate. Calculate the percentage purity of the sample of potassium chlorate used. The results obtained by this method are approximately 0.5 per cent. too high.

Ferrocyanides

Ferrocyanides can be titrated directly in acid solution by means of potassium permanganate, but it is not easy in this case to see a slight excess of this reagent. This difficulty can be avoided by adding excess of permanganate to the acidified ferrocyanide solution, and determining the excess by running in decinormal ferrocyanide, after the addition of a few drops of ferric sulphate solution, until a permanent bluish-green colour is obtained. So long as any permanganate remains in solution, the standard ferrocyanide added is at once oxidised to ferricyanide, which does not give a blue colour with a ferric salt.



Exercise.—Prepare 100 ml. of decinormal potassium ferrocyanide by dissolving 4.223 grams of the pure crystallised salt, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, in water and making up to 100 ml. Measure out 10 ml. of bench ferrocyanide solution, add about 60 ml. of dilute sulphuric acid, and run in decinormal permanganate from a burette until the liquid has a definitely red tinge. Add a few drops of a solution of ferric alum, and run in the decinormal potassium ferrocyanide with constant shaking until the solution acquires a bluish-green tint throughout. Calculate the normality of the bench ferrocyanide from the volume of potassium permanganate actually used for its oxidation.

STANDARD CERIC SULPHATE

(*N/10 solution contains 33.23 grams $\text{Ce}(\text{SO}_4)_2$ per litre*)

Cerium forms two series of salts, cerous and ceric, in which it is trivalent and quadrivalent respectively. Cerous salts are colourless, and can be oxidised to ceric salts, which are yellow or orange, by oxidising agents such as persulphates and sodium bismuthate. Ceric salts are reduced by ferrous salts, oxalates, nitrites, etc.

As an oxidising agent in volumetric analysis, ceric sulphate possesses the following advantages. It cannot be reduced below the cerous state, its titre remains constant for long periods in light or in air, and it is less affected by the presence

of hydrochloric acid than is potassium permanganate. When used for the oxidation of a colourless solution, the presence of a slight excess of ceric sulphate is detectable by its colour, though the change is less marked than when potassium permanganate is used. In the case of coloured solutions, however, an indicator is necessary to show the end-point of the reaction. There are several such indicators available. They are organic compounds, the oxidised forms of which differ in colour from the reduced forms. A fuller discussion of these indicators will be found on p. 220. As in the case of potassium permanganate, titrations are usually carried out in the presence of sulphuric acid.

The equivalent weight of pure crystalline ceric sulphate, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, is 404.3, but the commercial salt contains impurities. An approximately decinormal solution of ceric sulphate is prepared by adding 14 grams of the salt to 200 ml. of 2N sulphuric acid, and heating until the liquid is almost clear. The cooled solution is filtered into a 250 ml. flask and diluted to the mark.

The ceric sulphate solution must now be standardised by means of sodium oxalate, which is oxidised in acid solution in accordance with the equation



Weigh out accurately about 0.18 gram of sodium oxalate, which has been previously dried at 120° . Dissolve it in about 200 ml. of water, add 5 ml. of concentrated sulphuric acid, and heat nearly to boiling. Now run in ceric sulphate solution until the presence of an excess is indicated by a yellow colour. Allow the solution to stand for 5 minutes to ensure complete oxidation, cool the solution, add a drop of 0.025M *o*-phenanthroline indicator (see below), and titrate the excess of ceric sulphate with decinormal ferrous ammonium sulphate. Determine the ceric sulphate equivalent of the ferrous ammonium sulphate, and calculate the net consumption of ceric sulphate by the oxalate. Repeat the titration with another weighed portion of ceric sulphate.

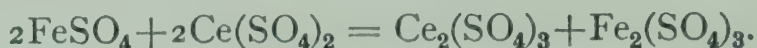
Oxalic Acid and Oxalates

a. Pure Iodine.

The procedure is described above under should be ground of ceric sulphate with sodium oxalate. and resublimed before

Iron

Iron must be present in the ferrous state, and if necessary the solution must first be reduced, preferably by zinc (p. 137). The equation for the reaction is



Since ferric sulphate has a slight colour, an indicator must be used to determine the end-point of the titration. Various indicators may be used for this purpose, the most satisfactory being *o*-phenanthroline; but *N*-phenylanthranilic acid, which is less expensive, may usually be substituted.

The *o*-phenanthroline indicator is prepared as follows:— Make up 7 ml. of a 0.025M ferrous sulphate solution by dissolving 0.05 gram of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 7 ml. of dilute sulphuric acid. Add 0.1 gram of *o*-phenanthroline (p. 221), and shake until all the solid is dissolved. One drop of this solution should be used for each titration. The change at the end-point is from red to almost colourless (pale blue).

If *N*-phenylanthranilic acid is to be used as indicator, prepare a 0.005M solution of its sodium salt by dissolving 0.106 gram in a little water containing about 0.05 gram of sodium carbonate, and diluting to 100 ml. About four drops of this solution are used for titration. The colourless solution goes pink at the end-point. Since the redox potential is 1.08 volt, the addition of a phosphate is unnecessary, as explained in the case of *o*-phenanthroline (p. 221).

If neither of these indicators is available, the titration may be carried out with diphenylamine or sodium diphenylamine sulphonate as indicator. These, however, are less satisfactory, since they tend to decompose in the presence of ceric sulphate. The details of their use are given on pp. 134 and 144.

500. **Procedure.**—Weigh out accurately about 1 gram of ferrous oxalate or ammonium sulphate, dissolve it in a mixture of 50 ml. of dilute sulphuric acid and 50 ml. of water. Add the appropriate amount of indicator and titrate with standard ceric sulphate. Below the column are given the volumes of 1/10 ceric sulphate corresponds to 0.005585 periods in light at 480 mμ.

Iodides

This determination depends upon the liberation of iodine, each atom of which displaces one atom of hydrogen from acetone which is present in excess. Mono-iodo-acetone is formed.



It will be seen that, because the iodine liberates an equivalent amount of hydrogen in an ionic form from the acetone, the equivalent weight of potassium iodide for this reaction is half its molecular weight.

Procedure.—Make up 100 ml. of M/20 potassium iodide solution by dissolving 0.830 gram of potassium iodide in water. Measure out 25 ml. of this solution into a 500 ml. flask, add 25 ml. of acetone, 35 ml. of dilute sulphuric acid, and dilute to about 100 ml. Add one drop of *o*-phenanthroline ferrous sulphate (see the determination of Iron above), and titrate with standard ceric sulphate solution until the red colour changes to a very pale blue. A brown colour, from free iodine, may develop in the liquid if the addition of the ceric sulphate is rapid, and the liquid must be stirred until this disappears before proceeding. The vapour of mono-iodo-acetone has an irritant effect on the eyes.

Ferrocyanides

Ceric sulphate oxidises ferrocyanides to ferricyanides according to the equation



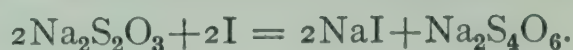
Make up an approximately decinormal solution of potassium ferrocyanide by dissolving 4.2 grams of the crystalline salt in water, and diluting to 100 ml. Measure out 25 ml. of this solution into a 600 ml. flask, add 250 ml. of water, and two drops of a solution of diphenylamine prepared by dissolving 0.1 gram in 10 ml. of concentrated sulphuric acid. Titrate with standard ceric sulphate until a deep blue colour

Pure Iodine.

should be ground
and resublimed before

Standard Sodium Thiosulphate and Standard Iodine

SODIUM thiosulphate is useful in volumetric analysis mainly on account of the manner in which it interacts with iodine, viz. :—



The process may be used for the determination of iodine itself and all substances (mainly oxidising agents) that will liberate iodine from potassium iodide, and is therefore capable of wide application.

Standard iodine solution is used as an oxidising agent for the determination of easily oxidisable substances, such as sulphurous acid, arsenic (as sodium arsenite), and tin (as stannous chloride). Sometimes the standard iodine and thio-sulphate solutions are used in conjunction.

In iodometric titrations an excess of potassium iodide must always be present to prevent any volatilisation of iodine, and the titration should be carried out in a flask. A dilute solution of starch is generally used as an indicator. This is a very sensitive reagent for minute traces of iodine, with which it gives an intense blue colour, provided that a soluble iodide is present. The blue colour disappears above 45° , but returns on cooling.

In cases where it is necessary to add acid to liberate iodine the hydrogen ion concentration should be kept as low as possible. Otherwise the hydriodic acid formed is liable to be oxidised by air to yield additional iodine. Acetic acid may always be used with safety, but the concentration of a mineral acid should not exceed 0.25 normal except in the absence of oxygen. When this concentration must be exceeded, oxidation may be prevented by forming a layer of carbon dioxide on the surface of the liquid by the addition of a little sodium bicarbonate.

sol.

Crystall.

STANDARD SODIUM THIOSULPHATE

As an solution contains 24.82 grams of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ per litre) possesses the molar weight (248.2 grams) of sodium thio- below the ~~crystalline~~ $5\text{H}_2\text{O}$, is equivalent to 126.9 grams of periods in light ~~and~~ (at ~~equation~~), a solution that contains 24.82

grams of the salt per litre is described as a decinormal solution. The so-called "pea-crystals" of photographic "hypo" are usually very pure, but when the salt is dissolved in ordinary distilled water it suffers slight decomposition and the concentration of the solution slowly alters, possibly because of the action of bacteria. It is a common practice to add a small amount of sodium carbonate or borax to preserve the solution, but the addition of either of these substances is undesirable. One objection is that the resulting solution is found to have a slightly different normality when it is used for titrating a standard substance in acid solution from that obtained when it is used in titrating the same or another standard substance in neutral solution. A litre of approximately decinormal solution which keeps well can be prepared by adding about 25 grams of pure sodium thiosulphate to about 950 ml. of water at the boiling-point, boiling for a few minutes, cooling, and making up to a litre with recently boiled and cooled water. Kassner and Kassner (*Ind. Eng. Chem., Anal. Ed.*, 1940, 12, 655) recommend the addition of 0.4 ml. of chloroform per litre as a preservative. This may be used in a solution prepared with water which has not been boiled, or as an additional precaution in a solution prepared as described above. The solution is standardised as described below. It should be kept in the dark, or in a stock bottle covered with brown paper to exclude light.

Preparation of the Starch-Indicator Solution.—Mix 1 gram of "soluble starch" with a little cold water, pour the mixture into 200 ml. of almost boiling water, and boil for about one minute. After cooling, the solution is ready for use. If "soluble starch" is not available, grind 1 gram of ordinary starch with a little cold water, pour the mixture slowly into 200 ml. of boiling water and boil for two minutes. Set aside for a few hours (or overnight) and decant the clear liquid. Starch solution will not keep in good condition for more than about two days unless it is sterilised, *e.g.* by adding either 5 ml. of dilute hydrochloric acid or 2 milligrams of mercuric chloride or iodide to the quantity mentioned above.

Standardisation of Sodium Thiosulphate with Pure Iodine.—Commercial iodine is often impure, and should be ground with a little solid potassium iodide and resublimed before

use.¹ On account of its volatility, iodine cannot be accurately weighed in the ordinary manner, and the following special method must therefore be adopted.

In a weighing-bottle place about 2 grams of pure potassium iodide with 10 *drops* of water. Allow to come to room temperature, wipe the outside dry, and weigh accurately. Add 0.3 to 0.4 gram of pure iodine, replace the stopper at once, and weigh again. This gives the weight of the iodine. When the iodine has dissolved, wash it rapidly into a flask containing about 1 gram of potassium iodide in about 200 ml. of water, and titrate *at once* with the sodium thiosulphate solution. When the iodine solution becomes very pale yellow in colour, add about 2 ml. of starch solution and continue the titration until the blue colour just disappears. Repeat the process with another weighed quantity of iodine and from the results calculate the normality of the thiosulphate solution.

The starch solution must not be added until near the end of the titration. If the volume of the iodine solution is not large, it is possible to complete the titration without using starch—except in artificial light.

Standardisation of Sodium Thiosulphate with Potassium Iodate.—Potassium iodate is easily obtained in a pure state, and may be used in standardising sodium thiosulphate. It is used in presence of an excess of potassium iodide and dilute hydrochloric acid, when the following reaction takes place :



The equivalent weight of potassium iodate is therefore one-sixth of its molecular weight.

Dry a few grams of potassium iodate at 120°, and prepare 250 ml. of a decinormal solution by dissolving 0.8918 gram in water, and making up in a graduated flask. To 25 ml. of water in a flask add 2 grams of potassium iodide, 0.5 gram of sodium bicarbonate, and 10 ml. of dilute hydrochloric acid.

¹ A small quantity of pure iodine may be prepared as follows :—Grind together in a mortar about 2 grams of iodine with about 0.2 gram of potassium iodide. Place the mixture in a small porcelain basin, cover with a round-bottomed flask containing cold water, and heat gently, so that the iodine sublimes slowly on to the flask. The iodine must then be dried by enclosing it in a narrow stoppered weighing-tube containing a little calcium chloride covered with a layer of glass-wool.

Run in 25 ml. of the iodate solution, and titrate the liberated iodine with the thiosulphate solution.

Standardisation of Sodium Thiosulphate with Potassium Permanganate.—If potassium permanganate is added to an acid solution of potassium iodide, the permanganate is reduced and an equivalent amount of iodine is liberated. A solution of sodium thiosulphate can therefore be standardised by titrating the iodine liberated from potassium iodide by a measured volume of standard potassium permanganate solution.



Dissolve about 2 grams of potassium iodide in 50 ml. of water in a 400 ml. flask, add 10 ml. of dilute sulphuric acid, about 0.5 gram of sodium bicarbonate, and 25 ml. of standard (decinormal) potassium permanganate. Allow to stand in the dark for five minutes, dilute to about 200 ml., and titrate the liberated iodine with the thiosulphate solution as described above.

A "blank" titration should be carried out using the same quantities of potassium iodide and sulphuric acid, and the thiosulphate reading subtracted from that obtained before.

Standardisation of Sodium Thiosulphate with Potassium Dichromate.—When potassium dichromate is added to an acid solution of potassium iodide, iodine is liberated according to the equation



If a standard (decinormal) solution of potassium dichromate is available, it may be used for the standardisation of the thiosulphate solution, the procedure being the same as with standard permanganate (see above). Instead of a standard solution, weighed quantities of potassium dichromate may be used. The method tends to give results that are slightly too high.

Dissolve about 2 grams of potassium iodide in 50 ml. of water, add 10 ml. of dilute sulphuric acid and about 0.5 gram of sodium bicarbonate. To this solution add 0.12 to 0.14 gram (accurately weighed) of potassium dichromate and allow to stand for five minutes in the dark. Then dilute to about 200 ml., and titrate the liberated iodine with the thiosulphate solution, using starch as indicator. At the conclusion of this titration the

solution is green in colour, on account of the chromic sulphate present. The colour change at the end-point—from blue to light green—is nevertheless easily observed if the solution is diluted to at least 200 ml.

An alternative method in which 5 ml. of glacial acetic acid are used in place of the sulphuric acid, together with 5 ml. of M/1000 copper sulphate solution as catalyst, is described by Dudley Sully [*J. Chem. Soc.*, 1942, 366]. It is necessary to deduct from the volume of sodium thiosulphate used an amount equivalent to that of the copper sulphate added.

The gram-equivalent of potassium dichromate is 49.03.

Standardisation of Sodium Thiosulphate with Pure Copper.

—This is described on p. 161.

STANDARD IODINE

(N/10 solution contains 12.69 grams per litre)

Iodine is almost insoluble in water, but it dissolves in a solution of potassium iodide. It is very volatile, and in both the preparation and use of a standard iodine solution, precautions are necessary to prevent loss by volatilisation. Commercial iodine is usually impure, and, even if pure iodine is available, it is difficult (on account of its volatility) to prepare an accurate standard solution by weight. It is preferable, therefore, to prepare an approximately decinormal solution from commercial (B.P.) iodine, and standardise it with a standard sodium thiosulphate solution, or by means of arsenious oxide or barium thiosulphate.

On a rough balance weigh 6.4 grams of powdered iodine and introduce it into a 500 ml. standard flask. Add 10 to 12 grams of potassium iodide (free from iodate), and *not more than 20 ml. of water*. Shake until all the iodine has dissolved, and then dilute to the graduation mark. Iodine dissolves quickly in a concentrated potassium iodide solution, but very slowly in a dilute solution, and much time will therefore be wasted if the solution is diluted before all the iodine has dissolved.

Standardisation with Arsenious Oxide.—The oxidation of arsenious oxide by iodine may be represented by the equation



The reaction is reversible, but the oxidation is quantitative if the hydriodic acid is neutralised as it is formed. Neither

sodium hydroxide nor sodium carbonate may be used for this purpose, since they interact with iodine, but sodium bicarbonate introduces no appreciable error if the solution is saturated with carbon dioxide. The hydrolysis of the bicarbonate is then very slight, and the solution at the end of the titration is approximately neutral.

Measure out from a burette (the solution is poisonous) 25 ml. of standard arsenious acid solution, prepared as described on p. 168, into a conical flask. Add 2 ml. of starch solution, and 15 ml. of a saturated solution of sodium bicarbonate (prepared in the cold). Run in iodine solution slowly from another burette until a permanent blue tint is just obtained throughout the solution.

The gram-equivalent of arsenious oxide is 49.45.

Standardisation with Barium Thiosulphate.—Weigh out accurately about 0.7 gram of finely powdered $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ into a beaker, and add about 100 ml. of water. Run in the iodine solution slowly with continuous stirring. When most of the sparingly soluble barium salt has reacted, add starch solution and complete the titration.

The gram-equivalent of barium thiosulphate is 267.5.

ANALYSES INVOLVING THE USE OF STANDARD IODINE AND STANDARD THIOSULPHATE

Copper

When a copper salt is mixed with a solution of potassium iodide, cuprous iodide is precipitated and iodine is liberated :



The amount of copper can therefore be found by titration of the free iodine. According to the equation, 1 gram of copper requires 5.22 grams of potassium iodide, but in practice a considerable excess of the latter is necessary ; if the solution to be titrated contains about 0.15 gram of copper—requiring about 25 ml. of standard (decinormal) thiosulphate—about 2 grams of potassium iodide should be added.

Arsenic, antimonie, and ferric compounds may interfere in this titration unless special precautions are taken. [*Ind. Eng. Chem., Anal. Ed.*, 1936, 8, 119.] If manganese is present,

care should be taken to acidify with acetic acid as soon as possible after neutralising with ammonia any nitric acid used in producing the copper solution. In alkaline solution divalent manganese is rapidly oxidised to a higher valency and this would result in the liberation of iodine on the subsequent addition of acetic acid.

Exercise.—The copper in a bronze coin, or in brass, may be determined by this method.

Clean a halfpenny with emery cloth, and cut it into four approximately equal pieces. Weigh one of the pieces accurately. Place the weighed piece in a 200 ml. conical flask, add 5 ml. of water and 5 ml. of concentrated nitric acid, and warm on the steam-bath until the alloy has dissolved (about twenty minutes). The small white residue of stannic oxide need not be filtered off, since it in no way interferes with the analysis.

It is essential that the solution to be titrated should contain no nitrite, and the following procedure must be closely adhered to. Dilute the solution with 25 ml. of water and boil it briskly for two minutes in order to expel oxides of nitrogen. Rinse the neck and side of the flask with a little water, and then add about 0.5 gram of urea¹ (in order to destroy traces of nitrous acid). Neutralise the nitric acid by adding ammonia (about 15 ml.) until a bluish-white precipitate forms. Then add dilute acetic acid more than sufficient to redissolve the precipitate (about 5 ml.). Cool, and dilute the solution to 250 ml. in a standard flask.

In a 200 ml. conical flask, dissolve 2 grams of potassium iodide in 20 ml. of water, and add 25 ml. of the copper solution. (Cuprous iodide is nearly white, but the free iodine colours the mixture brown.) Titrate the mixture with standard sodium thiosulphate until the brown colour becomes faint; then add 2 ml. of starch solution, and continue the titration until the mixture loses the last trace of a grey-blue tinge and appears almost white. In case traces of iodine have been adsorbed by the precipitate, it is advisable at this point to add about a gram of potassium thiocyanate to desorb them, and if the blue colour returns, discharge this by further addition of a drop

¹ Instead of urea, bromine-water may be added until the solution shows a slightly greenish tint. The excess of bromine is then removed by boiling until the issuing steam no longer produces a blue colour with potassium iodide-starch paper.

or so of thiosulphate. The end-point is quite sharply defined. After reading the burette, however, it will be found advantageous—until some experience has been gained—to add a few additional drops of the thiosulphate and to keep the mixture as a guide for a second titration.

The rapid reappearance of the blue colour soon after the titration is apparently finished indicates that the solution has not been completely freed from nitrite, and the determination will therefore be inaccurate.

Calculate the percentage of copper in the coin. One litre of normal thiosulphate corresponds to 63.54 grams of copper.

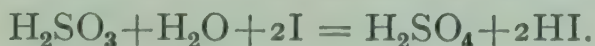
Standardisation of Sodium Thiosulphate with Pure Copper.

—If a solution of sodium thiosulphate is to be used mainly for the determination of copper, it is best to standardise it in the following manner:—Weigh accurately about 0.15 gram of pure (electrolytic) copper foil. Place it in a 200 ml. conical flask, add 1 ml. of water and 1 ml. of concentrated nitric acid, and warm the flask on the steam-bath until the copper has dissolved. Following the method detailed above, dilute the solution with 25 ml. of water, boil briskly for two minutes, and add 0.5 gram of urea (see footnote, p. 160). Then add ammonia until a precipitate forms, and redissolve the precipitate in dilute acetic acid. Cool, add 2 grams of potassium iodide, and titrate the mixture with the thiosulphate as described above.

Alternative Method.—Weigh accurately about 2.5 grams of pure copper sulphate. Wash it into a 100 ml. standard flask and dissolve in water. Add about 1 ml. of dilute ammonia and 5 ml. of dilute acetic acid, and dilute the solution to the mark. Measure 25 ml. of the solution into a conical flask, add 2 grams of potassium iodide, and titrate with the thiosulphate solution. (One litre of normal thiosulphate corresponds to 249.7 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.)

Sulphurous Acid and Sulphites

Sulphurous acid in dilute aqueous solution is oxidised by iodine to sulphuric acid according to the equation



The alkali sulphites are oxidised to sulphates in a similar manner. The sulphite solution is run into a measured excess of acidified iodine solution (not *vice versa*), with constant stirring,

and the residual iodine is then titrated with standard thio-sulphate. If the iodine is run into the sulphite solution, the reaction takes place in accordance with the above equation only when the sulphite solution is very dilute (about centinormal).

Exercise.—Determine the percentage of Na_2SO_3 in a sample of commercial sodium sulphite crystals. Weigh accurately from 2.5 to 2.8 grams of the crystals, dissolve in water, and dilute to 250 ml. in a standard flask.

Measure 25 ml. of decinormal iodine into a flask, add 5 ml. of dilute hydrochloric acid, dilute to about 100 ml., and add slowly 25 ml. of the sulphite solution. Titrate the excess of iodine with standard thiosulphate.

Hydrogen Sulphide

Hydrogen sulphide interacts with iodine in aqueous solution according to the equation



A measured volume of the hydrogen sulphide solution is run into excess of decinormal iodine, and the excess of the latter is then titrated with standard thiosulphate.

If the concentration of the hydrogen sulphide solution is more than about 0.025 normal, the precipitated sulphur encloses a portion of the iodine which is thereby protected from interaction with the thiosulphate; the titration is then inaccurate. Accordingly, after making a preliminary titration, the hydrogen sulphide solution must be diluted in a standard flask *with air-free water* in such proportions that 10 ml. of decinormal iodine will oxidise about 40 ml. of the sulphide solution.

Hydrogen Sulphide in Mineral Water.—In order to determine the amount of hydrogen sulphide in mineral waters, take a measured volume, say 5 ml. of decinormal (or centinormal) iodine, add starch solution and 2 grams of potassium iodide, and pour in the water from a measuring cylinder until the blue colour is discharged. Titrate back with decinormal (or centinormal) iodine. A correction is necessary for the amount of iodine required to produce a blue colour in absence of hydrogen sulphide. In order to determine this, add starch solution and 2 grams of potassium iodide to a quantity of

distilled water equal in volume to that of the mineral water used, and titrate with the iodine.

Exercise.—Determine the normality of a solution of hydrogen sulphide prepared by passing a slow stream of fine bubbles of the gas through water at room temperature for ten minutes. Measure out this solution from a burette.

Mercurous Mercury and Ferric Iron

Mercury can be determined when in the form of mercurous nitrate by means of standard iodine, and a standard solution of this salt may be used for the determination of iron in the ferric state (Bradbury and Edwards, *J. Soc. Chem. Ind.*, 1940, 96T).

Determination of Mercurous Mercury.—The mercurous solution is run into a measured volume of standard iodine which oxidises it to the mercuric state, red mercuric iodide being precipitated. Sufficient potassium iodide is added near the end-point to dissolve the mercuric iodide, and the titration is finished, adding starch solution when the colour is pale yellow. If the potassium iodide is added at the beginning of the titration, considerably more of the mercurous solution will have to be added before all the free iodine has been removed. It is advisable, however, to make a preliminary titration in which the potassium iodide is added at first in order to determine at what stage of the subsequent accurate titration the potassium iodide should be added. The final disappearance of the starch iodide colour is somewhat slow, passing through a bluish-green stage and it is therefore better not to add the starch solution until practically all the free iodine has gone. If too little potassium iodide is added, a slight yellow suspension appears near the end-point. This does not appreciably affect the result, but makes it more difficult to decide when the starch solution should be added.

Make up 250 ml. of an approximately N/10 solution of mercurous nitrate by dissolving about 7.3 grams of the salt (which usually contains mercuric nitrate) in a solution of nitric acid containing 13 ml. of the concentrated acid previously diluted to 250 ml., and after the solid has dissolved, make the solution up to 250 ml. with the acid, and mix.

Make a preliminary titration by measuring out 25 ml. of N/10 iodine into a small flask. Add 20 ml. of a solution

containing 10 grams of potassium iodide in 100 ml. of solution, and run in the mercurous nitrate with continuous shaking until the yellow colour of the free iodine just disappears. It is unnecessary to add starch solution, as the end-point will be incorrect and about 1 ml. too high. Note the volume of the mercurous solution required.

Now make an accurate titration by measuring out another 25 ml. of N/10 iodine into the same flask, and with constant shaking run in the mercurous solution until within 3 ml. of the reading in the preliminary titration. To the red suspension of mercuric iodide add 20 ml. of the potassium iodide solution and shake until the precipitate has completely dissolved. The solution should now be clear and contain a slight excess of iodine. The excess of iodine is then removed by further cautious addition of mercurous nitrate, shaking continuously and adding starch solution when the iodine colour has become quite pale. The final bluish-green colour should be discharged by one drop of the mercurous solution, allowing a short time after thorough mixing. Repeat the titration on another 25 ml. of iodine solution, and calculate the normality of the solution of mercurous nitrate. One litre of decinormal mercurous nitrate contains 20.06 grams of mercury.

Ferric Iron by Standard Mercurous Nitrate.—The reduction of a solution of ferric iron by mercurous nitrate in presence of a thiocyanate affords a convenient and a direct method for the determination of iron in the ferric state. If the iron is partly present in the ferrous state, this can be first titrated by potassium permanganate and the total iron then determined by mercurous nitrate. The chief advantage of the method lies in the much greater stability of mercurous nitrate as compared with that of the titanous salt solutions usually employed in a direct titration of ferric iron. Ammonium thiocyanate is used as indicator, and it is essential that not less than about 10 equivalents of this salt be present for each equivalent of iron. If less than this minimum proportion is used, a heavy precipitate forms and the red colour of ferric thiocyanate remains after the theoretical amount of mercurous nitrate has been added. An excess of thiocyanate is not harmful. The presence of dilute sulphuric acid does not interfere with the end-point, but the presence of hydrochloric acid necessitates the addition of slightly more than the theoretical amount of mercurous

nitrate. If, however, the final concentration of hydrochloric acid is not greater than about 0.2N the error is not more than 0.5 per cent.

Measure out 25 ml. of an approximately N/10 solution of ferric alum (see p. 137) into a 200 ml. stoppered bottle, and add 25 ml. of a solution of ammonium thiocyanate containing 20 grams in 100 ml. of solution. Run in mercurous nitrate solution while continually swirling the liquid in the bottle, until the colour becomes noticeably weaker. After this stage add the mercurous nitrate solution, a drop or two at a time, insert the stopper, and shake after each addition. A single drop will discharge the last tinge of red, but there should not be much delay in finishing the titration, as there is a tendency for the red colour to return. Repeat the titration on another 25 ml. of the ferric alum solution.

Dioxides, Chlorates, etc.

Substances that oxidise hydrochloric acid with evolution of chlorine may be accurately determined in the following manner. The method is specially useful for dioxides such as lead dioxide, red lead, and manganese dioxide, and as an illustration the determination of manganese dioxide in pyrolusite is described.

Valuation of Pyrolusite.—Manganese dioxide interacts with hydrochloric acid according to the equation



If the chlorine is passed into potassium iodide solution, it liberates an equivalent amount of iodine which may be determined by titration with standard sodium thiosulphate solution.

Reduce some pyrolusite to a fine powder by thorough grinding. In a small weighing-tube (1 cm. wide and 2 cm. long) weigh accurately from 0.10 to 0.15 gram of the powder, and introduce the tube and contents into a 200 ml. distillation flask (Fig. 36).

Fit the flask with a cork and glass tube, so arranged that a current of carbon dioxide from a Kipp apparatus can be passed into the flask and through the solution that is to be boiled in it. Connect the bent side-tube of the flask with a U-tube which contains 2 grams of potassium iodide dissolved in just sufficient water to fill the bend of the tube. As a precaution against incomplete absorption, connect with the U-tube a

tube full of glass beads wetted with potassium iodide solution. Place the U-tube in a basin of cold water.

When the apparatus is ready, pour 10 ml. of water and 20 ml. of concentrated hydrochloric acid into the flask, and replace the cork at once. Heat the mixture very gently, so that chlorine is slowly evolved. Gradually increase the temperature and finally heat until boiling, and pass a slow current of carbon dioxide through the boiling solution until all the chlorine is driven out of the flask (about ten minutes as a rule). In order to prevent the iodine and potassium iodide solution from passing back into the flask, increase the current of carbon dioxide

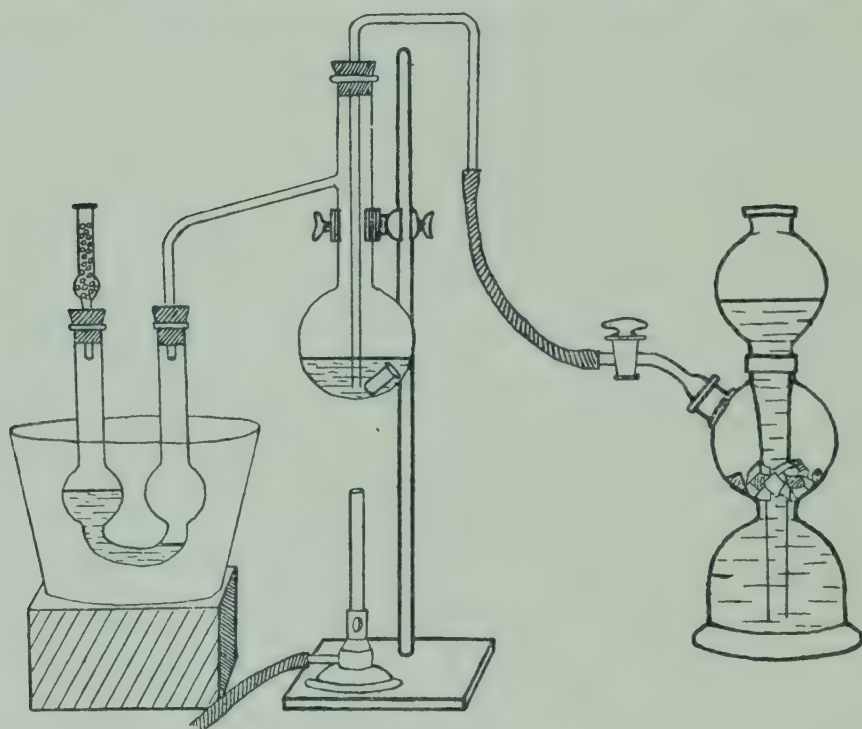


FIG. 36.

immediately the heating is stopped. (As pyrolusite invariably contains iron, the solution in the flask remains yellow at the end of the operation.)

Disconnect the absorption tube, wash the iodine and potassium iodide solution into a flask, and titrate at once in the usual manner with sodium thiosulphate.

Calculate the percentage of MnO_2 in the sample.

Lead Dioxide and Red Lead

The lead dioxide is mixed with a solution containing hydrochloric acid, potassium iodide, and a large excess of sodium chloride. The lead dioxide is converted into lead

iodide which dissolves in the excess of sodium chloride, and an equivalent amount of iodine is liberated :



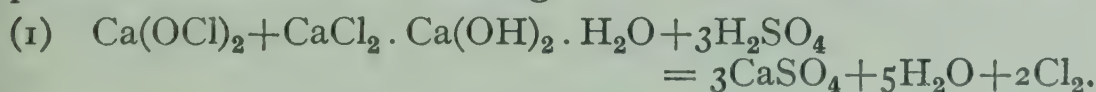
Place in a 200 ml. stoppered bottle 100 ml. of water, 20 ml. of concentrated hydrochloric acid, 1 gram of potassium iodide, and 20 to 25 grams of sodium chloride. Add 0.25 gram of *finely powdered* lead dioxide and shake vigorously for about two minutes. Titrate the liberated iodine with decinormal thiosulphate. Calculate the percentage of PbO_2 in the sample.

This method can also be used for red lead; 0.7 gram should be taken.

Available Chlorine in Bleaching-Powder

Bleaching-powder is now considered to be a mixture of calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, and a basic chloride, $\text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot \text{H}_2\text{O}$. Other substances, such as unchanged lime, calcium chlorate, and hydrated calcium chloride are also usually present as impurities. When treated with acid, the whole of the chlorine in fresh bleaching-powder, amounting to about 41 per cent., is liberated, and is therefore "available." The best commercial samples, however, seldom contain more than 35 to 39 per cent. of available chlorine. Bleaching-powder decomposes slowly on keeping, with formation of calcium chloride and chlorate, whilst exposure to atmospheric moisture and carbon dioxide results in loss of chlorine and hypochlorous acid. The available chlorine thus diminishes on keeping, and is no longer equal to the total chlorine (see p. 198).

The amount of available chlorine may be determined by mixing a solution of the bleaching-powder with excess of potassium iodide, and adding acid. The reactions are :—



The liberated iodine, which is equivalent to the available chlorine, is then titrated with standard thiosulphate. The procedure is as follows :—

Weigh accurately (in a stoppered weighing-bottle) about 2.5 grams of bleaching-powder. Bleaching-powder is not completely soluble in water; in order to obtain a uniform sample, it must be so finely ground that the insoluble portion

will remain for some time in suspension. Transfer the weighed sample to a glazed porcelain mortar, add 2 to 3 ml. of water, and grind to a smooth paste. Add more water gradually, then transfer the mixture completely to a 250 ml. standard flask and make up to the mark. Mix the contents of the flask by shaking, and repeat the shaking immediately before withdrawing each sample for titration.

Measure 25 ml. of the mixture into a 200 ml. flask, add about 1 gram of potassium iodide (10 ml. of a 10 per cent. solution), and excess of dilute acetic acid. Titrate the iodine with standard thiosulphate.

Failure to obtain a sharp end-point indicates partial disproportionation of the hypochlorite into chloride and chlorate. A sharper end-point will be obtained if sulphuric acid is used instead of acetic acid to acidify the solution.

Alternative Method.—The available chlorine in bleaching-powder may also be determined by means of standard arsenious acid (see p. 175).

Total Arsenic in Commercial Arsenious Oxide

Commercial arsenious oxide often contains some arsenic oxide as impurity. The following method of analysis is applicable also to mixtures of arsenious and arsenic salts.

Determination of Arsenious Oxide.—The arsenious oxide may be determined by the process already described for standardising a solution of iodine by means of arsenious acid (p. 158).

Weigh accurately about 1.2 gram of a sample of the commercial oxide. Dissolve in 10 ml. of warm sodium hydroxide solution, add 20 ml. of dilute hydrochloric acid, and make the solution up to 250 ml. in a standard flask.

Measure from a burette 25 ml. of the solution into a conical flask, add 10 ml. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine solution, using starch as indicator (p. 159).

Determination of Arsenic Oxide.—In strongly acid solution, arsenic acid is reduced by hydriodic acid to arsenious acid with liberation of iodine :



The reaction is complete within a few minutes if the solution is very strongly acid.

Evaporate 50 ml. of the arsenic solution (measured from a burette) until the volume is reduced to about 5 ml., cool, and pour into a 200 ml. conical flask containing 0.5 gram of sodium bicarbonate. Do not yet rinse the basin with water. Prepare a solution of hydriodic acid by dissolving 2 grams of potassium iodide in 10 ml. of water and adding 10 ml. of concentrated hydrochloric acid (free from chlorine). Rinse the basin into the flask with this solution without delay.

Cover the flask with a watch-glass, and set aside for at least ten minutes. Then dilute to about 50 ml., and titrate the liberated iodine with decinormal sodium thiosulphate *without* using starch indicator.

Antimony

Antimonious oxide interacts with iodine in the same way as arsenious oxide, and antimony may be determined by titration with a standard iodine solution in similar manner :



The hydriodic acid formed in the reaction must be neutralised by means of sodium bicarbonate as in the case of arsenic. In order to prevent precipitation of the antimony when an acid solution is diluted or neutralised, tartaric acid is added.

Antimony in Tartar Emetic.—Weigh accurately about 4 grams of tartar emetic and dissolve it in about 100 ml. of hot water. As the salt is a tartrate, the addition of further tartaric acid is unnecessary. Cool the solution and dilute it to 250 ml. in a standard flask. Measure 25 ml. into a conical flask, add 10 ml. of a saturated solution of sodium bicarbonate (p. 159), and titrate with decinormal iodine. Run the iodine solution down the side of the flask in order to avoid loss of carbon dioxide and use starch indicator as usual.

Antimony in Antimony Oxide.—Weigh accurately about 1.8 gram of antimony oxide. Dissolve the oxide by warming in a beaker with 5 ml. of concentrated hydrochloric acid, and then add about 5 grams of tartaric acid dissolved in a little water. Transfer the solution and the rinsings of the beaker to a 250 ml. standard flask, cool, and dilute to the graduation mark. Measure 25 ml. of the solution into a conical flask, add 25 ml. of a saturated solution of sodium bicarbonate, and titrate with decinormal iodine as described under tartar emetic.

In case the sample contains antimonious oxide, reduce the antimonious to antimonious chloride in another portion of the solution by adding about 1 gram of sodium sulphite (or by passing sulphur dioxide through the warm solution). Boil the solution gently for five minutes and then pass a current of carbon dioxide through the boiling solution until the sulphur dioxide is expelled. Cool the solution, add 25 ml. of sodium bicarbonate solution, and titrate with decinormal iodine.

Tin in an Alloy

Preparation of a Solution for Analysis.—Dissolve a weighed portion of the alloy (from 0.1 to 1 gram, according to the amount of tin) in concentrated hydrochloric acid with careful exclusion of air. This simple method, which dispenses with further reduction, is possible with some alloys such as solders and pewters, and is described on p. 417.

If the alloy is not completely soluble in hydrochloric acid alone, place it in a small flask on the steam-bath with 25 ml. of the acid and add about 0.5 ml. of bromine, or a few crystals of potassium chlorate, from time to time. When the sample is completely dissolved, support the flask in a water-bath at 65° to 70°, and pass a current of carbon dioxide or air through the solution until bromine or chlorine ceases to be evolved. It is advisable that the temperature should not exceed 70° during the passage of the gas, or stannous chloride may be lost by volatilisation.

If the alloy cannot be brought into solution by the method above, disintegrate it with nitric acid as described on p. 419, dilute to about 30 ml., filter, and wash the residue with hot water. Analyse the residue by the method given for an ore (p. 171), or for tin in bronze (p. 421).

Reduction and Titration.—The tin is reduced to the stannous condition by warming the solution containing hydrochloric acid with metallic iron or nickel, or by boiling it with metallic antimony. The stannous chloride is then determined by titration with standard iodine solution.

Stannous chloride is very readily oxidised by atmospheric oxygen, and it is essential, therefore, that the solution should be protected from contact with the air both before and during the titration. This is accomplished by keeping the flask filled with carbon dioxide.

Procedure.—(a) If copper, arsenic, or antimony is present, place the solution, diluted to 100 ml. and containing 25 per cent. by volume of concentrated hydrochloric acid, in a 300 ml. beaker. Place a clean iron rod or a coil of piano wire in the solution, cover with a clock-glass, and keep near the boiling-point for about thirty minutes or until the solution becomes colourless. (Copper, arsenic, and antimony are precipitated, and tin is for the most part reduced to stannous chloride.) Remove and rinse the iron, filter the solution into a 400 ml. flask, and proceed at once as described in (b).

(b) If copper, arsenic, and antimony are absent (or have been removed), place the solution in a 400 ml. flask fitted with a rubber stopper carrying a bent inlet tube for carbon dioxide, and a straight, wide tube, about 7.5 cm. by 8 mm. Add 50 ml. of concentrated hydrochloric acid and about 1 gram of antimony powder (*free from sulphide*), and dilute to 200 ml.

Pass a slow current of carbon dioxide through the flask, while heating on the water-bath for twenty minutes, and then boiling briskly for five minutes. Cool the solution by placing the flask in cold water, while passing a *rapid* current of carbon dioxide through the flask. Add starch solution and titrate with decinormal iodine. Run in the iodine solution through the straight tube without lifting the rubber stopper, and maintain a current of carbon dioxide through the flask during the titration.

The end-point in the titration is attained when a blue coloration persists throughout the solution. The blue coloration may subsequently disappear on account of further reduction by the antimony, but this occurs so slowly, in the cold, that it does not interfere with the titration.

Tin in an Ore

Preparation of a Solution for Analysis.—Fuse about 8 grams of potassium hydroxide in a spun iron crucible, and continue the heating until all moisture is expelled and quiet fusion attained. Cool, add about 0.5 gram (accurately weighed) of the finely powdered ore, cover the crucible, and heat, at first cautiously, and then with a full Bunsen flame until action ceases. Pour the molten mass into a clean nickel basin floating in a dish of water, and cover the hot mass with a crucible lid to prevent loss when the mass cracks during cooling.

Place the iron crucible in a porcelain basin, add 100 ml. of water, and boil. If any of the fused mass remains attached to the crucible, add a little hydrochloric acid, and assist the dissolution process by breaking off any adhering lumps with a glass rod. When the crucible is clean, remove and rinse it. Now add the cake detached from the nickel basin, and the crucible lid if there is anything attached to it. Add 30 ml. of concentrated hydrochloric acid and heat on a water-bath. There should be no undissolved residue from the ore, but there may be a few scales of ferric oxide from the crucible.

Transfer to a 400 ml. conical flask, add 30 ml. of concentrated hydrochloric acid, dilute to about 200 ml. with hot water, and proceed at once with the reduction and titration as described on p. 170.

Hydrogen Peroxide

Hydrogen peroxide slowly oxidises a solution of hydriodic acid, and may therefore be determined by titration of the iodine liberated :



This method is better than that described on p. 119, as the presence of organic compounds, often added to stabilise hydrogen peroxide, will lead to results which are too high if the permanganate method is used.

The hydrogen peroxide must be diluted in a standard flask until it is not more than 0.3 normal. Ten ml. of this solution are added with constant shaking to a solution of 2 grams of potassium iodide and 2 grams of sodium bicarbonate in 200 ml. of dilute sulphuric acid in a conical flask. After the mixture has been allowed to stand for five to ten minutes, the liberated iodine is titrated with thiosulphate, starch being added when the colour of the iodine has been nearly discharged.

Iron

Ferric salts may be determined without previous reduction, since in acid solution they liberate iodine on addition of potassium iodide, and this can be titrated with thiosulphate solution.



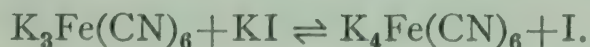
The reaction is slow at ordinary temperatures, but it can be accelerated by the addition of a catalyst such as cuprous

chloride or by heating. Heating would involve loss of iodine unless carried out in a closed vessel, but if the iodine which is liberated on standing for a few minutes at ordinary temperatures is first removed by running in thiosulphate, and the solution is then heated to 50° C. there is no appreciable loss of the small amount of iodine subsequently liberated. It is, however, necessary to displace the air in the titration flask by carbon dioxide to avoid high results, as an appreciable amount of iodine is set free by atmospheric oxygen, probably owing to oxidation of the ferrous salt formed. Sodium bicarbonate is therefore added to the acid solution.

Weigh out accurately about 4 grams of powdered ferric alum, and dissolve this in about 40 ml. of water containing 15 ml. of dilute sulphuric acid, and make up to 100 ml. in a graduated flask. Measure out 25 ml. of this solution into a 250 ml. flask, add 10 ml. of dilute sulphuric acid (hydrochloric acid may be used if free from dissolved chlorine), and dilute to about 60 ml. Now add 1 gram of sodium bicarbonate and 2 grams of potassium iodide, and at once fit a cork loosely into the flask, or plug with cotton-wool. Keep the flask in the dark for five minutes and then run in 0.1N thiosulphate until the free iodine has just disappeared, but do not add starch yet. Heat the solution to about 50° C. with the flask still loosely corked, and complete the titration, finally using starch solution.

Ferricyanides

Soluble ferricyanides react incompletely with potassium iodide, the following equilibrium being established :—



This reaction goes completely to the right if excess of zinc sulphate is added to precipitate the ferrocyanide as it is formed. The free iodine can be titrated with thiosulphate.

Exercise.—Weigh out accurately about 0.6 gram of potassium ferricyanide, and dissolve it in 50 ml. of water in a conical flask. Add 10 ml. of dilute hydrochloric acid, and about 2.5 grams of potassium iodide and 0.5 gram of sodium bicarbonate. When these have dissolved, add 2 to 3 grams of zinc sulphate (free from iron), shake well and allow to stand

for two minutes. Titrate the liberated iodine by means of thiosulphate, using starch as indicator.

Ammonium Salts by Bromine-Water

Ammonium salts may be rapidly determined by means of their interaction with bromine-water, if the acidity is correctly adjusted by the addition of sodium bicarbonate. The reaction is as follows :—



Excess of bromine-water is added, and the amount unused determined by titrating the iodine liberated by it from a solution of potassium iodide.

Procedure.—Determine the strength of a stock bromine-water roughly by adding 5 ml., from a burette or small measuring cylinder, to a solution of 2 grams of potassium iodide in water acidified with 5 ml. of dilute hydrochloric acid. Titrate the iodine liberated with a standard sodium thiosulphate solution (see p. 154). Make up in a stoppered flask 250 ml. of approximately 0.05 normal bromine-water by appropriate dilution of the stock. Loss of bromine from the solution during the subsequent titrations may be diminished by the addition of 5 to 10 grams of potassium bromide during dilution, but if care is exercised this precaution is not essential. Standardise the prepared bromine-water accurately by running 50 ml. from a burette into acidified potassium iodide solution, and titrating with thiosulphate.

Weigh out accurately about 0.5 gram of ammonium chloride, dissolve, and make up to 100 ml. in a standard flask. To 10 ml. of this solution in a conical flask add 50 ml. of water, and 3 grams of sodium bicarbonate. Run in bromine-water from the burette while shaking, until a definite yellow tint from excess of bromine is observed. Allow to stand for a few minutes. Add 2 grams of potassium iodide, and make the solution definitely acid with dilute hydrochloric acid, adding this carefully through a funnel in the mouth of the flask, the outside of the funnel being washed down into the flask after the evolution of carbon dioxide has ceased. Titrate the liberated iodine with sodium thiosulphate, and thence calculate the weight of bromine which was used in the reaction with ammonium chloride. From this the weight of ammonium chloride present may be found, remembering that from the equation 3Br is equivalent to NH_4Cl .

STANDARD ARSENIOUS ACID

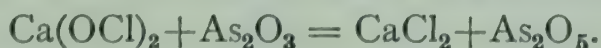
(N/10 solution contains 4.945 grams As_2O_3 per litre)

Standard arsenious acid is used as a reducing agent for the determination of available chlorine in bleaching-powder, hypochlorites, iodine, etc. It may also be used for standardising potassium bromate and potassium permanganate. It is prepared from arsenious oxide which, unless known to be pure, must be purified as follows :—Dissolve 10 grams of the commercial oxide in 50 ml. of warm concentrated hydrochloric acid. Add 100 ml. of water and set the solution aside overnight. Filter off the crystals of arsenious oxide that separate, wash them with a little cold water, and dry in a desiccator.

Weigh accurately in a small covered porcelain basin about 1.25 gram of pure arsenious oxide. Add 10 ml. of 20 per cent. sodium hydroxide solution and gently warm the basin, stirring the mixture until the oxide dissolves. Transfer the solution and the rinsings of the basin to a 250 ml. graduated flask. Add enough dilute hydrochloric acid to make the solution just acid to phenolphthalein, dilute to the graduation mark, and mix thoroughly.

Available Chlorine in Bleaching-Powder

This method depends on the oxidation of trivalent arsenic to the quinquevalent state by a hypochlorite. The reaction may be represented by the following (simplified) equation :—



Standard arsenious acid solution (see above) is run into the bleaching-powder solution from a burette, and the end of the reaction is determined by means of potassium iodide-starch paper ; so long as any hypochlorite remains undecomposed, a blue stain is produced on the test-paper when a drop of the solution is brought into contact with it. The procedure is as follows :—

Prepare a solution of the bleaching-powder in the manner described on p. 167. After shaking, measure 25 ml. of the turbid mixture into a small beaker and make a rough titration by running in the standard arsenious acid, rapidly at first, and then 0.5 ml. at a time, stirring continuously, until a drop of the solution gives no blue stain when placed on potassium iodide-starch paper.

Repeat the titration, only on this occasion remove no test drops until within about 1 ml. of the previously determined end-point. As the end-point is approached, the blue stain becomes less pronounced, and is last seen near the centre of the wet spot on the test-paper. The end-point is quite sharp.

Calculate the percentage of available chlorine in the bleaching-powder.

Preparation of Potassium Iodide-Starch Paper.—Grind 0.5 gram of starch with a little cold water, pour into 100 ml. of boiling water, boil for a minute, and cool. Add about 2 ml. of 10 per cent. potassium iodide solution. Dip strips of filter paper into the mixture and hang them over a glass rod until dry. Preserve the strips in a stoppered bottle.

STANDARD TITANOUS SULPHATE

(*N/10 solution contains 19.20 grams of $Ti_2(SO_4)_3$ per litre*)

Titanous salts are powerful reducing agents which may be used to determine a variety of substances, organic as well as inorganic, by volumetric methods. In presence of acid they reduce ferric salts to ferrous salts, chromates to chromic salts, and chlorates to chlorides; in alkaline solution nitrates are reduced to ammonia. Organic nitro-compounds, such as nitro-benzene and picric acid, are reduced to the corresponding amines; azo-compounds and dyestuffs like indigo are reduced and decolorised.

Many applications of titanous chloride as a quantitative reducing agent will be found in Knecht and Hibbert's *New Reduction Methods in Volumetric Analysis* (see Appendix, p. 529). Titanous chloride, however, oxidises rapidly in air, and standard solutions of this salt must be kept in an atmosphere of hydrogen, and titrations should be carried out in an atmosphere of inert gas. Instead of attempting to preserve a standard titanous solution, it is better to make up a solution of a titanium salt of arbitrary strength, and reduce a measured volume of this as required. Titanous sulphate has advantages over the chloride, in that it is less easily oxidised by air, and back-titrations can be carried out by means of potassium permanganate without difficulty.

"Titanous" sulphate is sold in the form of a solution which is rather less than normal. It contains titanous sulphate and

must always be reduced before use. Thirty millilitres of this solution diluted with 4N sulphuric acid to 250 ml. in a standard flask will give an approximately decinormal solution.

Standardisation of Titanous Sulphate.—Measure out 25 ml. of the diluted “titanous” sulphate solution into a 150 ml. stoppered bottle containing 100 grams of zinc amalgam, and add 25 ml. of 4N sulphuric acid. Replace the stopper and shake vigorously for at least one minute, in which time the deep brown colour of partially reduced titanium will have changed to violet. Pour off the aqueous liquid through a No. 3 sintered glass crucible into a filter-flask containing about 2 grams of sodium bicarbonate, and wash the amalgam twice with 4N sulphuric acid as described under the reduction of ferric alum (p. 140). To the titanous sulphate solution add 0.1 gram of potassium thiocyanate, and titrate it with decinormal ferric alum until the brownish-red tint produced is permanent. Warm the solution to 50° towards the end of the titration, placing the flask in a basin of water. The thick-walled filter-flask may be replaced by an ordinary Pyrex flask fitted with a rubber stopper bored with two holes, if only gentle suction is used. Such a flask may be heated directly.

Titanous sulphate, if free from iron, may also be standardised by means of potassium permanganate, in which case, after reduction, the titration may be carried out in the cold.

A special burette for use with titanous solutions has been described by Flaschka (*Mikrochem. Mikrochim. Acta*, 1951, 36-37, 269).

Iron

Determine the percentage of iron in iron wire by weighing accurately about 0.56 gram of the wire, and dissolving it in a mixture of 20 ml. of water and 5 ml. of concentrated sulphuric acid. Run in dilute potassium permanganate solution until the smallest possible excess is present, and make up to 100 ml. Pour this into a burette, and titrate against 25 ml. of titanous sulphate as described above.

Chlorate

Prepare an approximately decinormal solution of potassium chlorate by weighing out accurately about 0.205 gram, dissolving, and making up to 100 ml. Measure out 25 ml. into

a flask, and add about an equal volume of 4N sulphuric acid. Reduce 50 ml. of decinormal "titanous" sulphate by zinc amalgam as described on p. 177, and pour this into the chlorate solution. Warm to 50°, add 0.1 gram potassium thiocyanate, and titrate with decinormal ferric alum. If the titanous sulphate has been standardised by potassium permanganate, this reagent should be used to determine the excess, the small amount of chloride resulting from the decomposition of the chlorate being without effect on the permanganate.

Determination of Titanium in its Oxide or an Ore

Titanium may be determined by means of standard ferric alum, after dissolution and reduction of the sample. In the case of precipitated titanium oxide, dissolution can be effected by heating with concentrated sulphuric acid and ammonium sulphate, but in the case of ores such as rutile or ilmenite it is necessary to fuse with potassium pyrosulphate.

Determination of Titanium in Titanium Oxide—Weigh accurately about 0.7 gram of titanium oxide into a 250 ml. conical flask. Add 25 ml. of concentrated sulphuric acid and about 8 grams of ammonium sulphate. Heat with a small flame until the oxide has dissolved. After cooling, dilute with water and make up the solution to 250 ml. in a graduated flask. A trace of insoluble matter may be ignored, as it will probably be merely silica. Reduce 50 ml. of this solution by zinc amalgam, and titrate the titanous sulphate with decinormal ferric alum solution as described under the standardisation of titanous sulphate on p. 177.

Determination of Titanium and Iron in an Ore.—Grind the ore to a very fine powder in an agate mortar in small quantities at a time. Weigh accurately about 0.8 gram of the powder into a silica crucible, add about 6 grams of fused and coarsely powdered potassium pyrosulphate, and mix with a platinum wire. Fuse the mixture and extract the melt as described on p. 439, but use only 50 ml. of water instead of 100 ml. Filter to remove any white residue (which will consist of silica), wash with dilute sulphuric acid, and make up the filtrate to 100 ml. in a graduated flask. Determine the titanium in 25 ml. of this solution with ferric alum as described above.

The iron content of the ore may be determined by reducing

another 25 ml. of the solution with zinc amalgam and titrating with standard potassium permanganate. The iron is obtained by difference (the second titration represents the sum of the iron and titanium).

STANDARD POTASSIUM BROMATE

(N/10 solution contains 2.784 grams of $KBrO_3$ per litre)

Potassium bromate in hot acidified solution reacts with certain reducing agents forming potassium bromide. When the reducing agents have been completely oxidised, any excess of bromate reacts with the bromide liberating free bromine, the presence of which may be detected by methyl orange or other azo dyes, which are at once decolorised.

Titration with standard potassium bromate solution may therefore be used to estimate antimony and arsenic (after these have been brought to the tervalent state), stannous chloride, and certain metals when in the form of their compounds with 8-hydroxyquinoline ("oxinates"); also hydrazine and hydroxylamine.

Potassium bromate is easily obtained in a pure state, and is stable in solution. It is anhydrous, and should be dried at 120° before use.

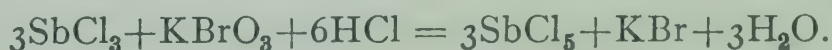
Weigh accurately 2.784 gram of pure potassium bromate, dissolve in water and dilute the solution to 1 litre in a standard flask. If the potassium bromate is not pure (bromide is a common impurity), the solution must be standardised in one of the following ways:—

- (1) Weigh accurately about 1.2 gram of pure arsenious oxide. Dissolve it in 10 ml. of warm sodium hydroxide solution (p. 175), transfer the solution to a 250 ml. standard flask, add 5 ml. of concentrated hydrochloric acid, and dilute to the graduation mark. To 25 ml. of the solution (measured from a burette) add 50 ml. of water and 20 ml. of concentrated hydrochloric acid. Titrate with the potassium bromate solution as described below under the determination of antimony.
- (2) Weigh accurately about 0.15 gram of pure, finely divided antimony, and transfer to a 250 ml. conical flask. Add 20 ml. of concentrated hydrochloric acid and a

few drops of bromine. Warm *very gently* until the antimony is dissolved, and then boil the solution until the excess of bromine is expelled. Reduce the antimonious to antimonious chloride and titrate with the potassium bromate solution as described below.

Antimony

When potassium bromate is added to a hot acid solution of antimonious chloride, the latter is oxidised to antimonious chloride :



If antimony is to be determined in presence of arsenic, the latter must be got rid of as indicated below. Tin, lead, silver, zinc, copper (less than 5 per cent.), and iron (less than 10 per cent.) do not interfere with the determination.

Procedure.—Place the weighed sample of the ore or alloy (corresponding to not more than 0.15 gram of antimony) in a 250 ml. conical flask, add 25 ml. of concentrated hydrochloric acid and about 0.5 ml. of bromine, and warm very gently until dissolved. Boil the solution to expel the excess of bromine.

Reduction of the Antimonious Chloride.—Add 3 to 4 grams of sodium sulphite, rinse down the side of the flask with a little warm water, and boil the solution in a fume cupboard until the volume is reduced to rather less than 10 ml. Any arsenic that may be present is reduced and volatilised together with the excess of sulphur dioxide. If the sample is known to contain more than 2 per cent. of arsenic, add 20 ml. of concentrated hydrochloric acid and 5 ml. of sulphurous acid solution, and boil down again. Then add 20 ml. of concentrated hydrochloric acid and 70 ml. of water.

Titration with Potassium Bromate.—Run in the potassium bromate slowly (about 20 ml. per minute), with continuous brisk stirring, until most of the antimony is oxidised. Then add 2 ml. of methyl orange and continue the titration until the colour of the indicator disappears. The end-point is sharply defined.

If the methyl orange is added at the beginning of the titration, its colour gradually fades before the end-point is

reached, and more indicator must then be added. A preliminary titration may be carried out in this way.

Exercise.—Determine the percentage of antimony in a sample of type metal (alloy of lead, antimony, and tin). Use about 0.5 gram of filings or thin foil.

Arsenic

Tervalent arsenic may be determined by means of standard potassium bromate as described above for antimony, except that the solution must not be heated, and no reduction with sulphite is necessary.

Using a burette, take 10 ml. of arsenious acid solution prepared as described on p. 175. Add 20 ml. of concentrated hydrochloric acid and 70 ml. of water, and run in the potassium bromate as described above.

Hydrazine

Hydrazine is oxidised by potassium bromate in a warm acid solution containing excess of potassium bromide. The resulting reaction may be represented by the equation $\text{N}_2\text{H}_4 + \text{O}_2 = \text{N}_2 + 2\text{H}_2\text{O}$. One litre of decinormal potassium bromate is equivalent to $\frac{32.05}{40}$ grams of hydrazine. An indicator

such as indigo may be used to locate the end-point, or excess of potassium bromate may be added and the excess determined by means of potassium iodide and standard thiosulphate.

Prepare 100 ml. of an approximately decinormal solution of hydrazine by weighing accurately about 0.2625 gram of the hydrochloride, $\text{N}_2\text{H}_4 \cdot 2\text{HCl}$, or about 0.3250 gram of the sulphate, $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$, dissolving it in water and diluting to 100 ml. in a graduated flask. Measure out 25 ml. of this solution into a flask, add 3 grams of potassium bromide dissolved in 20 ml. of water, and 20 ml. of concentrated hydrochloric acid. Heat to between 50° and 60° , and run in 0.1N potassium bromate until the liquid shows a faint yellow colour, and a drop removed by a glass rod gives a blue colour on potassium iodide-starch paper. The excess of bromate solution should be kept as small as possible to avoid loss of bromine. At once add 2 grams of potassium iodide, and quickly cool the

solution to room temperature. Note the volume of bromate solution added, and titrate the liberated iodine with 0.1N thiosulphate. Deduct the volume of the bromate solution equivalent to the thiosulphate used from the volume of the bromate added, and calculate the hydrazine.

Hydroxylamine

Hydroxylamine is slowly oxidised by potassium bromate in acid solution to nitric acid and water in accordance with the equation :



One litre of decinormal potassium bromate is equivalent to $\frac{33.03}{60}$ grams of hydroxylamine. It is necessary to add

excess of bromate and determine the excess by means of potassium iodide and standard thiosulphate.

Prepare 100 ml. of approximately decinormal hydroxylamine by weighing accurately about 0.116 gram of the hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$, dissolving it in water and diluting to 100 ml. in a graduated flask. Measure out 25 ml. into a 200 ml. bottle, and add about 20 ml. of water. From a burette add 40 ml. of 0.1N potassium bromate. Fit a rubber cork carrying a small glass tap, and evacuate the air from the bottle. Then add 20 ml. of concentrated hydrochloric acid through a small funnel connected to the tap, but do not allow any air to enter the bottle. Remove and wash the funnel, mix the contents of the bottle, and allow to stand for twenty minutes. Add 2 grams of potassium iodide dissolved in 10 ml. of water through the funnel and tap. Mix the solution, let air into the bottle, and titrate the liberated iodine with 0.1N thiosulphate. Deduct the volume of the bromate solution equivalent to the thiosulphate used from the 40 ml. of bromate added, and calculate the hydroxylamine.

STANDARD POTASSIUM IODATE FOR USE IN PRESENCE OF 4N HYDROCHLORIC ACID

(M/40 solution contains 5.350 grams KIO_3 per litre)

The use of potassium iodate in solutions strongly acidified with hydrochloric acid was proposed by Andrews in 1903.

It has been developed by Jamieson and others, and applied to the estimation of most reducing agents, and, indirectly, of oxidising and other substances.

The process depends on a series of reactions which take place consecutively in a solution about 4N with respect to hydrochloric acid. The potassium iodate is first reduced to potassium iodide, and this reacts with further potassium iodate to give free iodine. This is oxidised by still more potassium iodate to iodine *cations*, the ionised compound formed being iodine chloride.

Potassium iodate is easily obtained in a pure state, is stable in solution, and is unaffected by filter paper. The salt is anhydrous, and should be dried at 120° before use.

Make up 250 ml. of potassium iodate solution by dissolving 1.3376 grams of pure dry KIO_3 in water (M/40 grams per litre), and making up in a standard flask.

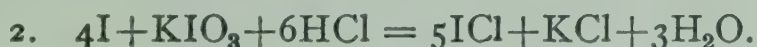
Iodides

If a solution of potassium iodate is added to one of potassium iodide containing *dilute* hydrochloric acid, the reaction takes place according to the following equation:—



This reaction has been referred to in the standardisation of hydrochloric acid (see p. 87), and of sodium thiosulphate (see p. 156).

If the concentration of hydrochloric acid present is sufficiently high, the free iodine is oxidised by additional potassium iodate, iodine chloride being formed, and this is only stable in a strongly acid solution:—



Combining these equations (multiplying (1) by 2, (2) by 3, and adding) and simplifying, the final equation for the reaction becomes:—



This reaction takes place in the presence of 12 per cent. or more of hydrochloric acid, but it is advisable to have the acidity of the solution not less than 4N at the end of a titration.

Procedure.—Make up a solution of potassium iodide by dissolving 1.66 grams in water, and diluting to 100 ml.

Measure out 10 ml. of the potassium iodide solution into a 250 ml. stoppered bottle, add 40 ml. of water, and 50 ml. of concentrated hydrochloric acid. Run in the iodate solution until the deep colour from the iodine liberated at first has become pale brown. Now add about 5 ml. of carbon tetrachloride or chloroform, stopper the bottle, and shake vigorously. If the layer of organic solvent is strongly coloured, add about another millilitre of the iodate solution, and repeat the shaking. When the purple colour of the solvent has become pale, the iodate solution is added drop by drop, shaking after each addition, until the colour is completely discharged. The aqueous layer will remain yellow owing to the presence of iodine chloride. Should the end-point be overshoot, a small measured volume of the iodide solution may be added, and the end-point redetermined.

From the equation deduced above, $\text{KIO}_3 \equiv 2\text{KI}$; so that
 1 ml. of M/40 $\text{KIO}_3 \equiv \frac{2 \times 166.0}{40000} = 0.00830 \text{ KI}.$

Copper

Copper is precipitated from a solution of its sulphate as cuprous thiocyanate, which is then titrated in presence of 4N hydrochloric acid with potassium iodate. The equation for the reaction is :—



Procedure.—Weigh accurately about 0.35 gram of copper sulphate, dissolve in water, and make up to 100 ml. in a standard flask. Measure out 25 ml., and precipitate the copper as thiocyanate (see p. 342). Filter through a filter paper, and place the washed precipitate with the paper in a wide-mouthed stoppered bottle. Add 50 ml. of water, and an equal volume of concentrated hydrochloric acid. Titrate with potassium iodate, finishing the titration as described under the estimation of iodides above.

Lead Dioxide

Lead dioxide and other oxidising agents can be determined by treating with excess of potassium iodide in the presence of 4N hydrochloric acid, and titrating the excess of potassium iodide with potassium iodate.

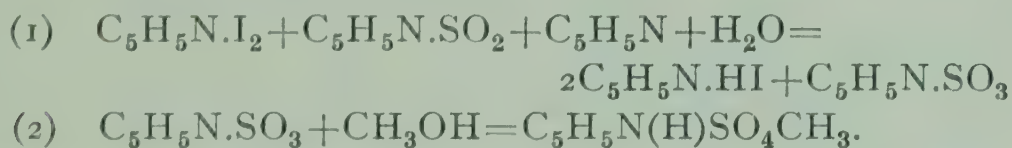
In the case of lead dioxide, the reaction is as follows :—



Procedure.—Weigh out accurately about 0.4 gram of lead dioxide, and wash this into a stoppered bottle. Add 25 ml. of decinormal potassium iodide, and a volume of concentrated hydrochloric acid about equal to the volume of liquid already in the bottle. Stopper and shake until the lead dioxide has dissolved. Now titrate with potassium iodate solution as described under the estimation of potassium iodide (p. 184). Knowing that PbO_2 is equivalent to KI (from the equation above), calculate from the excess of potassium iodide found, the percentage of lead dioxide in the sample taken.

KARL FISCHER REAGENT

The Fischer reagent is used for the determination of water in a wide variety of organic and inorganic substances. It consists of iodine, sulphur dioxide, pyridine, and methanol. The overall reaction involves two steps :



The reaction apparently involves a simultaneous oxidation and reduction of two components of the reagent by water. The end-point may be detected by the appearance of the colour of free iodine when excess of reagent has been added, or by an electrometric method. The method is subject to interference by a number of inorganic and organic compounds, but it is usually possible to circumvent the interference. It is probably the most widely-applicable method for the determination of moisture.

For suggestions for exercises see Mitchell, *Anal. Chem.*, 1951, 23, 1069.

Precipitation Processes

STANDARD SILVER NITRATE

(N/10 solution contains 16.99 grams AgNO_3 per litre)

STANDARD silver nitrate solution is used mainly for the determination of chloride, following either (1) Mohr's method of direct titration with potassium chromate as indicator, or (2) Fajans's method of direct titration with fluorescein or other adsorption indicator, or (3) Volhard's method in which the silver nitrate is used in conjunction with a standard solution of potassium (or ammonium) thiocyanate, with a ferric salt as indicator. The first and second methods are applicable only if the chloride solution is neutral. Volhard's titration is carried out in an acid solution and is of wider application. The same standard solutions of silver nitrate and potassium thiocyanate may also be used for the determination of bromide, iodide, and cyanide; chlorate, bromate, and iodate; silver and mercury.

A solution made by dissolving 16.99 grams of pure silver nitrate in water¹ and diluting to 1 litre is accurately decinormal. If ordinary commercial silver nitrate is used, an approximately decinormal solution is prepared (17 grams per litre) and is standardised with pure sodium chloride.

Standardisation of Silver Nitrate Solution.—If the silver nitrate is to be used in accordance with Volhard's method, it must be standardised by the method described on p. 194; if Mohr's or Fajans's method is to be followed, the solution is standardised as described below.

Dry the sodium chloride by heating it in a porcelain basin, or fuse it in a platinum basin and break up the fused mass. Weigh accurately about 1.45 gram of the salt, dissolve it in water, and dilute the solution to 250 ml. in a standard flask. Titrate 25 ml. of the solution with the silver nitrate, as described in the next paragraph.

Titration of a Chloride Solution by Mohr's Method.—This method, in which potassium chromate is used as an indicator, is based on the fact that silver chromate is much more soluble than silver chloride (25 mg. as compared with

¹ It is essential that distilled water be used throughout all silver and halide determinations.

1.5 mg. per litre at 18°). If silver chromate, which is bright red, is shaken with sodium chloride solution, it is immediately converted into silver chloride; and if silver nitrate solution is added to a solution of sodium chloride containing a little potassium chromate, practically all the chloride will be precipitated as silver chloride before any silver chromate (recognised by its red colour) is permanently formed, and the end-point of the chloride precipitation is thereby indicated. The chloride solution must be neutral or very faintly alkaline, because silver chromate is readily soluble in dilute acid. If the solution is acid, it is usually permissible to neutralise it by adding a slight excess of pure calcium carbonate, which should be used instead of sodium carbonate or hydroxide, as these usually contain chloride unless prepared by either of the methods described on p. 91.

Dilute 25 ml. of the chloride solution to about 70 ml. in a porcelain basin, and add 1 ml. of a 2 per cent. solution of neutral potassium chromate (free from chloride). The side-shelf reagent (0.2N) is suitable. If the solution contains chloride, add a few drops of silver nitrate, and filter. Make a 1 ml. pipette (Fig. 29, p. 83) for measuring the potassium chromate solution. Run the silver nitrate slowly into the chloride solution, with constant stirring. Silver chloride is precipitated, and a red precipitate of silver chromate also forms locally, but disappears on stirring. After all the chloride is precipitated, however, the addition of more silver nitrate produces a permanent precipitate of silver chromate. Continue the titration, therefore, until a *faint* reddish-brown tinge persists even after brisk stirring. Until some experience has been gained, it is a common mistake to add too much silver nitrate. After completing the first titration, it is advisable, therefore, to destroy the reddish-brown coloration by adding a few drops of ammonium chloride and to keep the mixture (protected from daylight until required) as a guide for a second titration made in another similar basin. The first tinge of a permanent reddish-brown coloration is more easily observed by comparison with this mixture.

Before the permanent colour change that marks the end-point of this titration can be recognised, a certain minimum amount of silver chromate must be permanently formed, and a measurable excess of silver nitrate is required to precipitate

this minimum amount. The excess that is necessary depends on several factors, *e.g.* the solubility of silver chromate in the solution at the end-point, and the ability of the analyst to recognise slight colour changes. It is desirable to eliminate the personal factor as far as possible by making all determinations under the same conditions, *e.g.* amount of indicator, and volume of solution at the end-point. The unavoidable error amounts to, in general, at least 1 drop (about 0.05 ml.) of silver nitrate, *i.e.* at least 0.2 per cent. if the titration requires about 25 ml. of silver nitrate. No correction need be made, however, if when standardising the silver nitrate solution it can be arranged that approximately the same volume of silver nitrate (25 ml.) will be required when determining the amount of chloride in a solution, since in that case the titration errors will balance out.

Titration of a Chloride in Neutral Solution by Fajans's Method.—In this method the sodium salt of fluorescein plays the part of an indicator, but in a manner essentially different from that of potassium chromate in Mohr's process. If freshly precipitated silver chloride, after having been carefully washed, is suspended in a solution of sodium fluoresceinate, it retains its white appearance. If, now, a drop of silver nitrate solution is added to the suspension, the silver chloride at once becomes red in colour. The explanation of the colour change is as follows :—The fine particles of silver chloride readily adsorb either halide ions (already present) or silver ions (added as silver nitrate) whichever are in excess. In the former case they become negatively charged and in the latter positively charged. When, therefore, excess of silver nitrate is present, the particles can then adsorb the negatively charged fluorescein anions ; this causes the particles to change colour on account of the formation of red silver fluoresceinate on their surface. It must be carefully observed that the adsorption of the fluorescein ion by silver chloride and the resulting colour change occur only when an excess of silver ion is present in the solution surrounding the silver chloride.

If, therefore, silver nitrate solution is slowly added to a solution of sodium chloride containing fluorescein, no colour change is observed until the precipitation of the chloride is complete and a minute excess of silver nitrate has been introduced. At this point, the suspended silver chloride becomes

pale pink, and the colour change marks the end-point of a titration by Fajans's method. Substances like fluorescein, the action of which as indicators depends on the phenomenon of adsorption, are described as "adsorption indicators." The indicator used for the titration of a chloride by this method is a 0.03 per cent. solution of the sodium salt of fluorescein,¹ and 1 ml. of the solution is taken for every 25 ml. of silver nitrate required. The chloride solution must be neutral or very faintly alkaline.

It must be noted that the colour change occurs, not in the solution, but on the surface of the silver chloride particles. It is more easily seen while the mixture is being stirred. The end-point is sharply defined and the titration error is almost negligible—not more than 0.1 per cent. (Compare Mohr's method.) A sharper end-point is obtained if the titration is completed somewhat rapidly, so that part, at least, of the silver chloride remains colloidal at the end-point. If the precipitate is completely coagulated, the adsorbing surface is much reduced and the colour change is evident only on the surface of the flocculated precipitate and is not apparent in the mixture as a whole.

Measure 25 ml. of the standard sodium chloride solution into a porcelain basin, add an equal volume of water and 1 ml. of the indicator solution. Run the silver nitrate slowly into the chloride solution, with constant stirring. (The precipitated silver chloride remains colloidal at first but coagulates freely near—at about 1 ml. short of—the end-point.) Continue the titration, meanwhile stirring continuously but not violently, until a permanent pink colour is suddenly observed in the turbid mixture.

The end-point is more readily perceived if the coagulation of the silver chloride has been entirely prevented by the addition of a solution of starch.

Repeat the above titration, adding, instead of 25 ml. of water, 10 ml. of water and 15 ml. of a freshly prepared 1 per cent. solution of starch.

If the concentration of the chloride solution is less than 0.01N, a sharp end-point is not obtained when fluorescein is used, and Fajans's method with this indicator is therefore not applicable to very dilute solutions of chlorides.

¹ This salt is sold as "soluble fluorescein."

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE

Chloride, Bromide, and Iodide

Mohr's Method.—The chlorides and bromides of sodium, potassium, magnesium, and calcium, in neutral solution, may be determined by titration with standard silver nitrate, using potassium chromate as indicator. The procedure is described on p. 187. In the case of barium chloride it is necessary (since barium chromate is insoluble) to precipitate the barium by adding sufficient potassium sulphate. The precipitated barium sulphate does not interfere with the titration.

For iodides the method is unsatisfactory and should be avoided.

Fajans's Method.—The titration of the chlorides of sodium and potassium by this method, using fluorescein as an adsorption indicator, is described in the preceding section. In presence of bivalent cations like calcium and magnesium, which cause immediate coagulation of the silver chloride precipitate, starch must be added to obtain an accurate result (see p. 189).

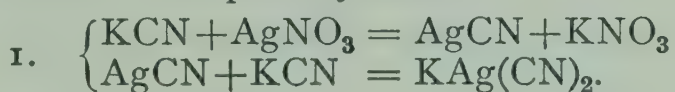
The bromides and iodides of sodium and potassium may be determined by the same method, the colour change at the end-point being very sharp, especially if the sodium salt of eosin is used. The titration of chlorides with this indicator is not possible, since silver chloride adsorbs eosin before the end-point is reached. A 0.05 per cent. solution of "soluble eosin" is prepared, and 1 ml. is used for every 25 ml. of decinormal silver nitrate required in the titration. Coagulation of the silver bromide occurs within 0.1 ml. of the end-point, and at the end-point the precipitate becomes brick-red. The colour change is much sharper than with fluorescein, and the titration error is negligible. With this indicator, bromide can be titrated in faintly acid solution (less than 0.1N acetic acid) with even greater precision than in neutral solution, and accurate results can be obtained with very dilute solutions (0.001N). Bromide cannot be titrated in presence of divalent cations with either fluorescein or eosin without the addition of one-third of the final volume of 1 per cent. starch solution (see p. 189).

Dichlorofluorescein (1 ml. of a 0.01 per cent. solution in 70 per cent. alcohol) may be used for the titration of chlorides, bromides, and iodides in neutral or weakly acid solutions, and

may therefore be used in the titration of salts which undergo slight hydrolysis, such as the chlorides of copper and zinc. This indicator is more acidic in character than fluorescein, and its ions are more readily adsorbed by the silver halides. It is therefore much more suitable than fluorescein for the titration of a very dilute solution of halides.

Cyanide

When silver nitrate is added to a solution of an alkali cyanide, it produces, locally, a precipitate of silver cyanide which, however, dissolves in the excess of the alkali cyanide and forms a soluble complex cyanide :



After all the cyanide has been converted into this complex salt, the addition of more silver nitrate produces a permanent precipitate of silver cyanide :



The cyanide in a solution may therefore be determined by titration with standard silver nitrate until a *permanent* precipitate is produced. This indicates that all the cyanide has been converted into the complex salt, and marks the beginning of reaction 2. The addition of a few drops of potassium iodide makes the end-point sharper. In presence of ammonium salts, silver cyanide is not precipitated, and potassium iodide *must* be added as an indicator.

Procedure.—Add 10 ml. of dilute ammonium hydroxide and a few drops of potassium iodide to the cyanide solution contained in a beaker, and dilute the mixture until the concentration of the cyanide solution is less than 0.02 normal. Place the beaker on a sheet of *black* paper, and run the standard silver nitrate slowly into the cyanide solution, with constant stirring, until the first permanent opalescence appears.

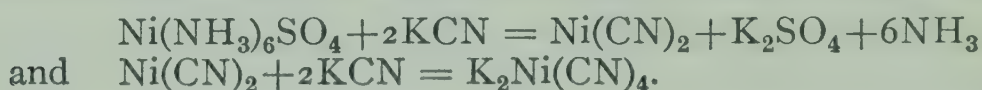
One molecule of silver nitrate corresponds to *two* molecules of potassium cyanide, *i.e.* 1 ml. of normal silver nitrate corresponds to 0.1302 gram of potassium cyanide.

Exercise.—Determine the percentage of potassium cyanide in a sample of commercial cyanide. Weigh accurately 3 to 3.5 grams, dissolve in water together with about 2 grams of sodium hydroxide, and make up to 250 ml. in a standard flask. Measure

with a burette 25 ml. of the solution for each titration, add 100 ml. of water and a few drops of potassium iodide solution. The commercial practice is to express the result as so much per cent. of *potassium* cyanide. As commercial cyanide is often mainly *sodium* cyanide, many samples give a "percentage" considerably above 100.

Nickel

When a solution of a nickel salt is made alkaline with ammonium hydroxide, and potassium cyanide is gradually added, the insoluble nickel cyanide first formed dissolves in excess of potassium cyanide forming a soluble complex cyanide.



The presence of excess of potassium cyanide may be detected by the disappearance of the precipitate, but more distinctly if a few drops of potassium iodide solution and a small measured volume of standard silver nitrate are added at the start of the titration. These reagents give a suspension of silver iodide which only disappears when an excess of potassium cyanide has been added. The end-point of the titration is found by running in one or more drops of the silver nitrate solution until a faint opalescence appears, from the formation of silver cyanide. The volume of potassium cyanide equivalent to the total silver nitrate added must be deducted from the volume of potassium cyanide used.

Cobalt interferes in this determination of nickel, but iron, aluminium, zinc and manganese may be present if sufficient sodium pyrophosphate is added. Chromium, if present, should be oxidised to chromate. The following solutions are required:—

Potassium Cyanide.—Dissolve about 4 grams of the salt, which must be pure, in water and dilute to 250 ml.

Silver Nitrate.—This solution must be of accurately known concentration, about 0.03N being most suitable.

Potassium Iodide.—Dissolve about 1 gram in 10 ml. of water.

Procedure.—Weigh accurately about 1.5 gram of nickel ammonium sulphate, dissolve this in water and make up the solution to 100 ml. in a graduated flask. Standardise the potassium cyanide solution by means of the standard silver nitrate solution as described in the determination of cyanide,

and calculate the volume of potassium cyanide solution which is equivalent to 1 ml. of silver nitrate. Now measure out 25 ml. of the nickel solution, add about 100 ml. of water and 1 gram of ammonium chloride to prevent the formation of a precipitate on making the solution alkaline. Add 10 ml. of dilute ammonium hydroxide, 1 ml. of the potassium iodide solution and run in 1 ml. of 0.03N silver nitrate (or less of a stronger solution) from a burette. Then run in the potassium cyanide solution from another burette while stirring or shaking until the precipitate, after increasing at first, finally disappears. Finish the titration by running in one or more drops of silver nitrate until the solution shows a faint turbidity. Note the volumes of the silver nitrate and potassium cyanide solutions added, and deduct from the latter the volume equivalent to the total silver nitrate used. Calculate the weight of nickel in the original solution, remembering that four gram-molecules of potassium cyanide are equivalent to one gram-atom of nickel.

STANDARD SILVER NITRATE AND STANDARD POTASSIUM THIOCYANATE

When potassium thiocyanate is added to silver nitrate, a white precipitate of silver thiocyanate is produced. In order to mark the end-point, a ferric salt (free from chloride) is added to the silver solution. No ferric thiocyanate is permanently formed until all the silver is precipitated as thiocyanate, and the appearance of a permanent brownish coloration (ferric thiocyanate) shows when precipitation is complete. The titration must be performed in acid solution, and nitric acid is therefore added to the silver solution. Since nitrous acid gives a colour with a thiocyanate solution, all the dilute nitric acid used in these titrations should be boiled to remove nitrous acid.

The thiocyanates of the alkalis are deliquescent salts, and a standard solution cannot be prepared by weighing a definite quantity. An approximately decinormal solution is therefore made by dissolving about 10 grams of potassium thiocyanate (or 8 grams of ammonium thiocyanate) in a litre of water. A solution of silver nitrate (approximately decinormal) is also required, and is made by dissolving 17 grams in 1 litre of water (see p. 186). These solutions are standardised as described below.

Preparation of the Indicator Solution.—Dissolve 5 grams of iron alum in 50 ml. of water, add 5 ml. of concentrated nitric acid (free from chloride), and boil the solution vigorously to expel oxides of nitrogen. Use 5 ml. of the solution for each titration.

Titration of Silver Nitrate with Potassium Thiocyanate.—The thiocyanate solution must be run into the silver nitrate solution, not *vice versa*. To 25 ml. of the silver nitrate contained in a porcelain basin add 5 ml. of the indicator solution, 10 ml. of dilute nitric acid, and then run in the thiocyanate slowly, with constant stirring. The first tinge of a permanent brown coloration marks the end-point. The brown coloration, which must persist after *brisk* stirring, is more easily seen if the precipitate is allowed to settle. After completing the first titration, destroy the brown coloration by adding about 1 ml. of silver nitrate, and keep this mixture as a guide for a second titration made in another similar basin (*cf.* p. 187).

After the silver nitrate solution has been standardised (as described in the next paragraph), the normality of the thiocyanate solution may be calculated.

Standardisation of the Silver Nitrate (*Volhard's Method*).—Weigh accurately 0.13 to 0.14 gram of pure, dry sodium chloride, and dissolve in 20 to 30 ml. of water in a small stoppered bottle. Add about 10 ml. of dilute nitric acid and 25 ml. of the silver nitrate solution. Shake the bottle vigorously until the precipitate coagulates and leaves the supernatant liquid clear. Filter¹ through a small paper into a porcelain basin. Rinse the bottle and wash the precipitate with cold water until all the silver nitrate is removed.² To the filtrate and washings add the ferric indicator, and titrate with thiocyanate.

¹ If the silver chloride is not removed by filtration, the end-point of the subsequent titration is indefinite and inaccurate, because silver chloride interacts with ferric thiocyanate and is converted into the *less soluble* silver thiocyanate. Pure potassium bromide (0.27 to 0.28 gram) may be used instead of sodium chloride for the standardisation and has the advantage that filtration is unnecessary, because silver bromide is less soluble than silver thiocyanate.

² To avoid washing the precipitate free from silver nitrate, the precipitation may be carried out in a standard flask, and an aliquot portion of the liquid taken for titration, after filtering through a dry filter and rejecting the first 10 ml. or so of the filtrate.

Calculation.—It was found that 24.1 ml. of a thiocyanate solution were required for 25 ml. of a silver nitrate solution.

Of this silver nitrate, 25 ml. were added to 0.1320 gram of sodium chloride, and the filtrate required 1.21 ml. of the thiocyanate.

The excess of silver nitrate corresponds to 1.21 ml. of the thiocyanate $= 1.21 \times \frac{25.0}{24.1} = 1.25$ ml. of the silver nitrate solution.

The volume of the silver nitrate solution corresponding to 0.1320 gram of sodium chloride is, therefore, $25 - 1.25 = 23.75$ ml.

The silver nitrate is, therefore, $\frac{1000 \times 0.1320}{23.75 \times 58.46}$ normal,
 $= 0.0951N$.

Separation of the silver chloride is avoidable, since its interaction with ferric thiocyanate (referred to in the footnote on p. 194) may be almost entirely prevented by the addition of 1 ml. of nitrobenzene for each 0.05 gram of chloride ion present before the addition of standard silver nitrate. The tightly stoppered bottle is then shaken for one minute, after which it will be found that the silver chloride has coagulated and carried down most of the nitrobenzene in such a manner that it not only protects the silver chloride from the action of the ferric thiocyanate, but also inhibits its darkening in the light. After addition of the ferric indicator, the excess of silver nitrate is slowly titrated with thiocyanate while the contents of the bottle are constantly swirled. The addition of the thiocyanate must be continued until the red colour persists for several minutes.

ANALYSES INVOLVING THE USE OF STANDARD SILVER NITRATE AND STANDARD THIOCYANATE

Chloride, Bromide, and Iodide

Chloride.—The determination of a chloride is carried out in a manner exactly similar to the method of standardisation described above.

To the chloride solution, acidified with nitric acid, add a measured volume of standard silver nitrate in *slight* excess,

and shake or stir the mixture vigorously until the silver chloride coagulates and settles. Filter the silver chloride, and wash it with cold water. (If care has been taken to use quite a *small* excess of silver nitrate, very little washing is required.) Titrate the excess of silver nitrate in the filtrate with thiocyanate.

Exercise.—Determine the concentration of the dilute hydrochloric acid on the bench. Dilute 10 ml. to 250 ml. in a standard flask, and titrate portions of 25 ml. as described above.

Bromide.—In this case it is unnecessary to filter off the silver bromide before titrating the excess of silver nitrate, since the interaction of silver bromide with ferric thiocyanate is negligible. Otherwise the procedure is the same as for chloride.

Iodide.—When silver nitrate is added to an iodide solution, the precipitated silver iodide retains a considerable amount of the soluble iodide or of the silver nitrate, and an error in the titration results. This may be lessened by dilution and shaking. The procedure must therefore be modified as follows :—

To a measured volume of the iodide solution, contained in a stoppered bottle, add dilute nitric acid, and dilute to about 250 ml. Add standard silver nitrate gradually from a burette, 1 to 2 ml. at a time, and after each addition insert the stopper and shake the bottle vigorously. Continue the addition of silver nitrate until a slight excess is present, when the precipitate coagulates and the supernatant liquid becomes clear. Then add 5 ml. of the ferric indicator, and, without filtering, titrate the excess of silver nitrate with standard thiocyanate.

Chlorate

The chlorate is reduced to chloride by gently boiling with a considerable excess of sulphurous acid solution, or by saturating the cold solution with sulphur dioxide and then boiling for about five minutes. The excess of sulphur dioxide is then expelled by passing a current of carbon dioxide through the boiling solution for about twenty minutes, and the chloride in the solution is determined in the usual manner with standard silver nitrate and thiocyanate.

If there is any chloride in the chlorate, a separate portion of the solution must be titrated without previous reduction, and the amount of chloride so found must be deducted from the titre representing the chlorate plus chloride.

Exercise.—Determine the percentage of potassium chlorate in a sample of the commercial salt. Weigh accurately about 2.8 grams, dissolve in water, and dilute to 250 ml. in a standard flask. Use 25 ml. for each titration.

Silver

Silver may be determined by titration of a solution with standard thiocyanate in the usual manner. With the exception of mercury, the presence of other metals does not, as a rule, interfere with the titration.

Exercise.—Clean a piece of silver weighing about 1.5 gram, *e.g.* a silver sixpenny piece, with emery cloth and weigh it accurately. Place it in a 200 ml. conical flask, add 5 ml. of water and 10 ml. of concentrated nitric acid, and warm gently until the coin is dissolved. Add a little water, and boil for five minutes in order to expel oxides of nitrogen. Dilute the cold solution to 100 ml. in a standard flask, and use 25 ml. for each titration.

Mercury

Mercury can be determined in the same manner as silver by titration with standard thiocyanate. The solution must contain a considerable excess of nitric acid, and the mercury must be present as mercuric nitrate. The reaction which occurs during the titration is as follows :—



As mercuric thiocyanate is somewhat soluble in water, it may not be precipitated ; but as it does not ionise appreciably this does not interfere with the titration, and no ferric thiocyanate is permanently formed until the reaction above is completed.

Procedure.—Weigh out accurately into a 300 ml. flask about 0.25 gram of mercury in the form of metal, oxide, or nitrate, and dissolve it in hot concentrated nitric acid diluted with an equal volume of water. Boil for a short time, cool, and make the solution faintly pink by the addition of decinormal potassium permanganate solution. Just discharge the pink colour by the cautious addition of very dilute ferrous

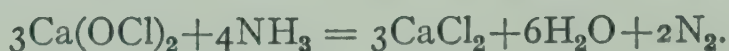
sulphate. Add 5 ml. of concentrated nitric acid, 5 ml. of ferric alum indicator, and titrate with standard thiocyanate until a faint permanent brownish tint is obtained.

Exercise.—Determine by the method above the percentage of mercury in mercuric oxide.

Total Chlorine in Bleaching-Powder

Besides “available” chlorine, bleaching-powder may contain chlorine as chloride and chlorate which are useless for bleaching purposes (see p. 167). In order to determine the total chlorine, prepare a solution of the bleaching-powder in the manner described on p. 167, and proceed as follows:—

Hypochlorite and Chloride.—Measure 25 ml. of the solution into a beaker, add 10 ml. of dilute ammonia, cover the beaker, and boil gently for about five minutes. The hypochlorite is thus converted into chloride, and nitrogen is liberated:



Add excess of dilute nitric acid, carefully avoiding loss through effervescence, and boil until free from carbon dioxide. Add excess of decinormal silver nitrate (25 to 30 ml.), stir until the precipitate coagulates, filter, and wash. Titrate the excess of silver nitrate in the filtrate with standard thiocyanate in the usual way.

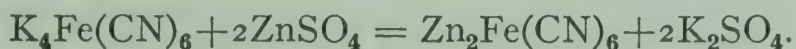
Hypochlorite, Chloride, and Chlorate.—Boil 25 ml. of the solution with dilute ammonia as before. Cool the solution and saturate with sulphur dioxide in order to reduce any chlorate to chloride. Boil for five minutes. Acidify with dilute sulphuric acid and expel the excess of sulphur dioxide by passing carbon dioxide through the boiling solution. (The last trace of sulphur dioxide may be destroyed by carefully adding dilute potassium permanganate until the solution is faintly pink.) All the chlorine in the bleaching-powder is now present in the solution as chloride, which may be determined by means of standard silver nitrate and thiocyanate in the usual manner.

The percentage of total chlorine in the bleaching-powder may then be calculated, and also (by difference) the percentage of chlorine present as chlorate. If the available chlorine in the same sample has been determined (pp. 167 and 175), the amount of chlorine which is present as chloride may also be calculated.

STANDARD POTASSIUM FERROCYANIDE

Zinc

When potassium ferrocyanide is added to an acid solution of a zinc salt, zinc ferrocyanide is first precipitated :



The addition of more potassium ferrocyanide converts the zinc ferrocyanide into the zinc potassium salt, and the complete reaction may be represented by the following equation :—



The completion of the reaction may be determined by means of an external indicator—a solution of uranium nitrate. The use of an external indicator may be avoided by the addition of diphenylamine to the acidified zinc solution. This indicator, in the presence of ferricyanide accompanied by a zinc salt in solution, forms blue oxidation products, which are reduced by the least excess of ferrocyanide after all the zinc has been precipitated. Enough ferricyanide is usually present in ferrocyanide which has not been freshly prepared, but it is advisable to add a small amount if a new solution of ferrocyanide is being made up. As the ferrocyanide is run into the zinc solution, a blue colour is produced which at the end-point changes to a permanent greenish-yellow. If the end-point is accidentally passed, a standard solution of zinc sulphate may be used for back-titration.

It will be seen from the equation that the formula weight of potassium ferrocyanide is equivalent to 1.5 gram-atoms of zinc, so that a normal solution of ferrocyanide for the purpose of this reaction contains one-third of a gram-molecule of this salt in a litre.

The standardisation of the potassium ferrocyanide and the actual determination of the zinc should be carried out under as nearly as possible the same conditions. Oxidising and reducing substances, and other metals giving insoluble ferrocyanides, *e.g.* copper, cadmium, iron, cobalt and nickel, must be absent. Small amounts of lead and aluminium do not interfere.

The following solutions are required :—

Potassium Ferrocyanide.—Make up 250 ml. of approximately N/5 potassium ferrocyanide by dissolving 7.0 grams of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, and 0.075 gram of potassium ferricyanide,

in water and making up to 250 ml. in a standard flask. One ml. of this corresponds to about 0.0065 gram of zinc.

Standard Zinc Sulphate.—Make up 250 ml. of N/5 zinc sulphate by weighing out 7.189 grams of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, dissolving in water and making up to 250 ml. in a standard flask.

Indicator.—Dissolve 0.1 gram of diphenylamine in 10 ml. of concentrated sulphuric acid.

Standardisation of Potassium Ferrocyanide Solution.—Measure out 25 ml. of the zinc sulphate solution, add 20 ml. of 4N sulphuric acid, 5 to 10 grams of ammonium sulphate, and 50 ml. of water. Add not more than 3 drops of the diphenylamine solution, and titrate with the ferrocyanide in the cold. The greenish-yellow colour when first obtained may revert to blue on standing, and ferrocyanide must be added drop by drop until it is permanent.

Exercise.—Determine the percentage of zinc in a sample of commercial zinc oxide (zinc white). Weigh accurately about 2 grams of the oxide. Dissolve in 25 ml. of 4N sulphuric acid, dilute the solution to 250 ml. in a standard flask, and titrate 25 ml. containing the same amounts of ammonium sulphate and sulphuric acid as indicated above.

This method can be applied to the determination of zinc in ores, after precipitating the zinc as sulphide. This is dissolved in 10 ml. of concentrated hydrochloric acid and 90 ml. of hot water. The hydrogen sulphide liberated must be expelled by boiling, after which the solution is just neutralised by ammonia. The procedure as given under the standardisation of potassium ferrocyanide is then followed.

Naphthidine as Indicator.—The use of naphthidine as an indicator in the titration of zinc with ferrocyanide has been described by Belcher and Nutten (*J. Chem. Soc.*, 1951, 548). The colour change of the indicator is reversible (from white to pink-red) and there is no indicator correction. The end-point is sharp to one drop, and is more easily detected than is the case when diphenylamine is used as indicator.

STANDARD POTASSIUM IODATE

Barium

The barium salt solution is treated with a measured excess of standard potassium iodate. The solution and precipitated

barium iodate are transferred to a standard flask, made up to the mark, and the excess of potassium iodate determined in an aliquot part by adding excess of potassium iodide, acidifying, and titrating with standard sodium thiosulphate.

Prepare a standard solution of potassium iodate by weighing accurately about 3.2 grams of pure potassium iodate, dissolving this in about 75 ml. of water, and making the solution up to the mark in a 100 ml. standard flask.

Determine the percentage of barium in crystalline barium chloride by weighing accurately about 0.2 gram of the salt and dissolving it in 20 ml. of water in a 100 ml. beaker. Support a dropping-tube (p. 261) so that the drawn out tip touches the side of the beaker well above the surface of the liquid and heat the solution to the boiling-point. Keep the liquid gently boiling and with a pipette run 25 ml. of the standard potassium iodate through the dropping-tube while stirring the liquid in the beaker. When the pipette has drained for fifteen seconds, remove it and wash the dropping-tube several times with small quantities of water. Boil the liquid gently for a minute while stirring and allow it to cool to room temperature. Transfer the liquid and precipitate to a 100 ml. standard flask, carefully washing the beaker, stirring rod, and funnel with small quantities of water. Make up to the mark with water and mix. After one hour filter the solution through a small dry filter, neglecting the first few millilitres which pass through the filter.

Titrate an aliquot part of the filtrate as follows :—Dissolve 2 grams of potassium iodide in 25 ml. of water, add about 0.5 gram of sodium bicarbonate, and 10 ml. of dilute sulphuric acid. Run in 10 ml. of the filtrate with a pipette, and titrate the liberated iodine by means of approximately N/10 sodium thiosulphate. Repeat the titration on another 10 ml. of the filtrate. Now standardise the sodium thiosulphate solution by taking another 25 ml. of the original potassium iodate solution and diluting it to 100 ml. in the standard flask used above. Mix, and titrate 10 ml. of the diluted solution exactly as described in the determination of the excess of potassium iodate in the filtrate from the barium iodate.

If W = the weight of KIO_3 in 25 ml. of the standard solution,

V_1 = the volume of $\text{Na}_2\text{S}_2\text{O}_3$ required to titrate 10 ml. of the filtrate,

and V_2 = the volume of $\text{Na}_2\text{S}_2\text{O}_3$ required to titrate 10 ml. of the diluted standard KIO_3 ,

then 1 ml. of $\text{Na}_2\text{S}_2\text{O}_3$ is equivalent to $\frac{W}{10V_2}$ grams of KIO_3 .

The weight of KIO_3 used in precipitating barium is equivalent to $(10V_2 - 10V_1)$ ml. of $\text{Na}_2\text{S}_2\text{O}_3$ and is therefore

$$W \left(1 - \frac{V_1}{V_2} \right) \text{ grams.}$$

$$\text{Thus the weight of Ba precipitated} = \frac{137.4W}{2 \times 214} \left(1 - \frac{V_1}{V_2} \right).$$

STANDARD BARIUM CHLORIDE

Sulphate

Sulphates in acid or neutral solution can be determined by means of standard barium chloride, using a solution of sodium rhodizonate as indicator. This indicator gives a red coloration with a solution of a barium salt, whilst if a solution of a sulphate is added in excess the solution is yellow if neutral or nearly colourless if acid. The indicator may either be added to a measured volume of the standard barium solution, or it may be applied to a filter paper and drops of the solution being titrated tested by placing them on the treated paper. If the first method is used it is essential to run the sulphate into the barium solution containing the indicator, and this procedure is preferable if the indicator is used externally. If sulphite is present, excess of formaldehyde must first be added.

Prepare a solution of the indicator by dissolving 0.02 gram of sodium rhodizonate in 10 ml. of water. This must be freshly made up as the solution does not keep. Filter paper moistened with the reagent and stored in an evacuated desiccator over calcium chloride will remain effective for a few days.

Exercise.—Prepare 250 ml. of decinormal barium chloride solution and 100 ml. of a decinormal solution of sodium

sulphate. Measure out 25 ml. of the barium chloride solution, add 5 to 8 drops of the indicator and run in the sulphate solution from a burette until the red colour changes to yellow. Now repeat the titration without adding the indicator, and when an amount of the sulphate solution has been added within 0.5 ml. of that previously required place a drop of the liquid on a filter paper moistened with the indicator solution. A red stain should be produced by the barium still in solution, but on continuing the titration a point will be reached when a drop no longer gives a red stain.

Determine the concentration of an approximately decinormal solution of sulphuric acid as described above. In this case the yellow colour is discharged in the spotting test when all the barium has been precipitated.

STANDARD THORIUM NITRATE

Fluoride

Fluorides may be determined by a method depending on the fact that thorium fluoride is precipitated when thorium nitrate is run into a dilute solution of a fluoride at a suitable pH . The end-point is indicated by the formation of a pink colour when excess of thorium has been added to the fluoride solution containing sodium alizarin sulphonate.

The following solutions are required :—

(1) **Thorium Nitrate Solution.**—Prepare an approximately decinormal solution by dissolving 3.44 grams of thorium nitrate in water, and diluting to 250 ml.

(2) **Sodium Alizarin Sulphonate.**—Dissolve 0.05 gram of this indicator in 100 ml. of water.

(3) **Buffer Solution.**—Dissolve 4.724 grams of mono-chloroacetic acid in 25 ml. of N sodium hydroxide, and dilute to 50 ml.

(4) **Standard Ammonium Fluoride Solution.**—Dissolve 0.4868 gram of pure ammonium fluoride in water, and dilute to 250 ml. One ml. of this solution contains 1 mg. of fluorine.

Standardisation of Thorium Nitrate Solution.—Measure out 50 ml. of the ammonium fluoride solution into a conical flask, add 50 ml. of water, and 12 drops of the indicator solution. Make the mixture alkaline (pink) by adding a drop of normal

sodium hydroxide, and then just discharge the pink colour by careful addition of decinormal hydrochloric acid. Add 1 ml. of the buffer solution to produce a pH of approximately 3, swirl the solution, and add the thorium solution until a faint permanent pink colour is visible. Fifty ml. of the fluoride solution should require 26.3 ml. of $N/10$ thorium nitrate solution. A blank experiment should be carried out on 100 ml. of water containing the same amounts of indicator and buffer solution as above.

Exercise.—Determine the percentage of fluorine in sodium or potassium fluoride, using a solution containing approximately 1 mg. of fluorine per ml.

Complex-Forming Processes

DISODIUM ETHYLENEDIAMINETETRA-ACETATE

ONE of the most versatile volumetric reagents discovered in recent years is disodium ethylenediaminetetra-acetate (which will be referred to as EDTA). This reagent is the most interesting of the group of aminopolycarboxylic acids investigated by Schwarzenbach and his co-workers. It forms very stable metal chelates with many metals. Hydrogen ions are liberated during the formation of these complexes.

Two methods are available for the detection of the end-point of the reaction. In one, the hydrogen ions liberated may be titrated with standard alkali. In the other, use is made of a reagent, usually a dyestuff, which forms a coloured complex with the metal to be determined. The stability constant of this complex must be smaller than that of the complex formed by the metal with EDTA. The amount of this reagent that is added is small so that only a fraction of the metal ions present is combined in the coloured complex. As EDTA is added in the titration, it first combines with the free metal ions; eventually all the free metal ions, including those derived from the dissociation of the dyestuff complex, will have combined with EDTA. The dissociation equilibrium of the dyestuff complex will have been disturbed and more must dissociate. The metal ions that become available in this way will combine with more EDTA. The process will continue until the metal-dyestuff complex has been completely converted into the EDTA-metal complex, and the dyestuff has been liberated. If the colour of the dye is different from that of the metal-dyestuff complex, the appearance of the colour of the dyestuff can be used to detect the end-point of the reaction.

The metals for which methods have been developed include calcium, magnesium, zinc, iron, copper, thallium, silver, lead, nickel, and sodium. Methods have also been developed for the determination of phosphate and halogens. The method is particularly suited to the determination of the hardness of water.

It has been found that the end-point is not always easy to detect when complex-forming dyes are used as indicators. This difficulty may be overcome by performing the titration in a special cell in a spectrophotometer, and measuring the change in optical density during the titration, making the measurements

at a wavelength at which the free dye absorbs radiation but the metal-dye complex does not. In some cases it is possible to form a coloured complex which becomes colourless as the metal is extracted from it. In either case the principle is the same. During the titration the optical density of the solution changes as titrant is added, and finally assumes a constant value. The point at which it does so is taken as the end-point. (See Sweetser and Bricker, *Anal. Chem.*, 1953, **25**, 253.)

Magnesium

The following solutions will be required :—

Indicator Solution.—Dissolve 0.1 gram of Solochrome Black W DFA in 50 ml. of water. This solution must be freshly prepared each day.

Buffer Solution.—Dissolve 70 grams of ammonium chloride in 600 ml. of concentrated ammonia solution and dilute to 1 litre with distilled water. Store in a plastic bottle.

EDTA Solution.—Dissolve 4 grams of disodium ethylenediaminetetra-acetate dihydrate in water and dilute to 2 litres.

Standard Magnesium Solution.—Dissolve 0.2000 gram of pure magnesium metal in a few ml. of dilute hydrochloric acid. Evaporate the solution to dryness, dissolve the residue in water and dilute it to 2 litres. One ml. of this solution contains 0.100 mg. of magnesium.

Procedure.—Pipette 25 ml. of the standard magnesium solution into a 600 ml. tall form beaker, and dilute it to 300 ml. Add 10 ml. of buffer solution and 0.5 ml. of indicator solution. Stir the solution mechanically, and titrate with EDTA solution until the red colour changes to blue. Repeat the titration until close agreement between the results is obtained, and calculate the magnesium equivalent of the EDTA solution. Take a portion of the solution to be analysed such that it contains between 2 and 4 mg. of magnesium, and apply to it the procedure described above. Calculate the magnesium content of the sample. The EDTA complex of magnesium contains one molecule of EDTA and one magnesium ion.

POTASSIUM CYANIDE

The use of this reagent in complex forming reactions has already been described in the section on precipitation processes (see p. 191).

Electrometric Methods

ACIDIMETRY

REFERENCE has already been made (p. 77) to the determination of the hydrogen ion concentration of a liquid by means of electrical measurements, and to the detection in this way of the point of rapid change in pH which is found to occur whenever a stoichiometric point is reached in the titration of an acid by an alkali. Such methods, depending as they do on the observation of the movement of the needle of a galvanometer, are free from the personal factor involved in the matching of tints or the detection of changes in colour of a liquid, and are in addition applicable to cases in which the turbidity or original colour of the liquid makes the use of an indicator difficult. To determine the *absolute* value of the pH of a solution accurately by electrometric methods demands, however, meticulous care in the preparation of standards, and considerable technique in the carrying out of the experimental work, combined with expensive and possibly complicated apparatus, while unexpected sources of error are liable to affect the results. For the theory and practice of such determinations, special works must be consulted. But the detection of a considerable change in pH is a much simpler matter, and the stoichiometric point of a titration can be determined with an accuracy equal to that of ordinary volumetric analysis by the use of simple apparatus and the exercise of ordinary care. Similarly, approximate determinations of pH can be made, possibly useful in themselves, and certainly serving as an introduction to more exact work. Such simplified methods only will be dealt with here.

The Half-Cell, and its Potential

The reader will be familiar with the constitution and working of the ordinary simple electric cell, in which two metals immersed in a common solution produce an electric current when connected outside the cell. This current arises from a *difference* in potential between the two metals or electrodes which provides the electromotive force. Each of

the electrodes possesses by itself a potential which results from the tendency that exists for ions of the metal to pass into or out of the solution, a tendency that depends on the nature of the metal and of the solution with which it is in contact, and also on the concentration of the ions of the metal already present in the liquid. This potential is quite uninfluenced by the presence of the other electrode, and will remain the same if the cell is divided into two parts, leaving no connection either internally or externally between the two metals. Such an arrangement, consisting of a single electrode in a solution, is called a "half-cell." To obtain an electromotive force, this half-cell must be joined by a bridge or siphon of a conducting liquid to another half-cell containing either a different metal, or a different solution, or both. The E.M.F. generated by the combination may be determined by a calibrated potentiometer and galvanometer.

It will be seen from the above that the potential generated when a metal is immersed in a certain solution, though not capable of measurement by itself, may be determined when we combine the half-cell thus formed with another whose potential is already known, and then measure the E.M.F. generated by the pair; while to follow the change in potential from any alteration in the liquid of a half-cell, it is sufficient to combine it with any other half-cell whose potential remains constant during the period of the experiment.

To determine the actual pH of a solution, or to follow any change in its hydrogen ion concentration caused by the addition of a reagent, all that is required, therefore, is to use it as the liquid of a half-cell which has an electrode capable of receiving or giving up hydrogen ions, and to combine this half-cell, by means of a non-interfering "bridge" of conducting liquid with another half-cell whose potential is either known or constant. The potential of a hydrogen electrode in the presence of a normal concentration of hydrogen ions is taken as the standard to which all other half-cell potentials are referred; and hydrogen electrodes would seem to be desirable in the half-cells. The difficulty of handling hydrogen gas as an electrode can be overcome by adsorbing the gas by means of finely divided platinum on a foundation of platinum wire or foil, the platinum black being kept saturated with hydrogen by continuously bubbling the gas past it.

The hydrogen electrode formed in this way, however, though simple in theory, is rather troublesome in practice, and is very sensitive to adventitious influences, so that wherever possible some substitute is used. As a standard half-cell, a calomel electrode is almost universally employed, in which there is an electrode of mercury in contact with a solution of potassium chloride saturated with calomel, the potential of such an arrangement under definite conditions being known accurately. Where, again, a solution is acid and free from oxidising and reducing substances and from ammonium salts, the addition to it of a little quinhydrone gives with an electrode of clean platinum an almost perfect substitute for the hydrogen electrode. In the presence of oxidising agents the hydrogen electrode cannot be employed, and should theoretically be replaced by one of oxygen. Instead of this an electrode consisting of a metal and its oxide—antimony has been found the most suitable—may be used.

TITRATION OF ACIDS

In the case of a titration it is not necessary to measure the pH absolutely, but only to decide the point of maximum change in pH for the addition of a definite small amount of reagent. The standard half-cell may therefore be replaced

Complete Cell

Half-cell with changing potential: <i>e.g.</i> platinum electrode in acid liquid being titrated after addition of quinhydrone.	Bridge of conducting solution.	Half-cell with fixed potential: <i>e.g.</i> platinum electrode in solution of a salt after addition of quinhydrone. ¹
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¹ This salt solution is preferably buffered (see p. 308, footnote) to prevent changes in pH during the experiment from carbon dioxide from the air or alkali from the glass.

by any half-cell which gives a constant value ; and the procedure consists in investigating by means of a potentiometer, which need not be standardised, and a sensitive galvanometer, the potential difference generated by a cell built up as shown in the table above.

The following apparatus is required :—

Platinum Electrodes.—To make a platinum electrode a piece of narrow soft glass tubing about 15 cm. in length is

drawn out to a capillary, and this is cut off short. A platinum wire about 1 cm. long is pushed into the narrow opening so that half projects outside, and the glass is melted round the wire, the end being gently blown out so that the glass is of regular thickness. It is annealed by cooling slowly a few inches above the flame. Contact between the wire and the outside circuit is made by means of a little mercury poured into the tube into which a clean copper connecting wire can be dipped. Before use the platinum is cleaned by dipping into chromic acid mixture (p. 58), and then rinsing with distilled water. In use the wire only should be immersed in the liquid.

Quinhydrone, which in titrations of acids may be added to the liquid, is a slightly soluble crystalline organic compound of a complex character, which in a solution of pH less than 8 gives with a platinum wire a potential which depends on the concentration of hydrogen ions present. A little of the solid, sufficient to leave some undissolved, is stirred into the solution in which the platinum electrode is inserted. The final potential is reached in about a minute.

Connecting Bridge.—It is necessary to connect the two solutions in the half-cells by a conducting liquid, and a difficulty is met with in the fact that a diffusion potential is always set up at the junction of solutions which differ either in composition or concentration. Since this potential depends on the speed of migration of the ions, it may be almost nullified by selecting as a connecting medium the solution of a salt of which the positive and negative ions have approximately the same speed. Potassium chloride solution is most commonly used.

The simplest form of bridge is a glass siphon with short arms. The potassium chloride solution, which is conveniently of normal strength, may be retained in the siphon by plugging the ends of the tube with cotton-wool. It is more convenient to use siphons filled with an agar jelly, which is made by heating about 1 gram of agar in 30 ml. of the potassium chloride solution on a steam-bath for about an hour, filling the siphons, and leaving to stand until set. Contraction may be allowed for by fitting short pieces of rubber tubing onto the ends of the siphon, and removing these with any excess jelly afterwards. Such bridges may be used many times. They are washed with distilled water before and after use, and kept in the potassium chloride solution.

Electrical Instruments.—Results of a sufficient degree of accuracy may often be obtained by the use of a sensitive galvanometer alone, combined with a control resistance in series which can be cut out gradually. No actual readings of the swing of the needle can be taken, for the instrument must be used only to detect the point when no current flows from the combined half-cells, one of which contains the solution being titrated, and the other a solution of the salt which is formed by the reaction being studied.

To follow the course of the titration it is necessary to use a potentiometer, the simplest form of which consists of a wire

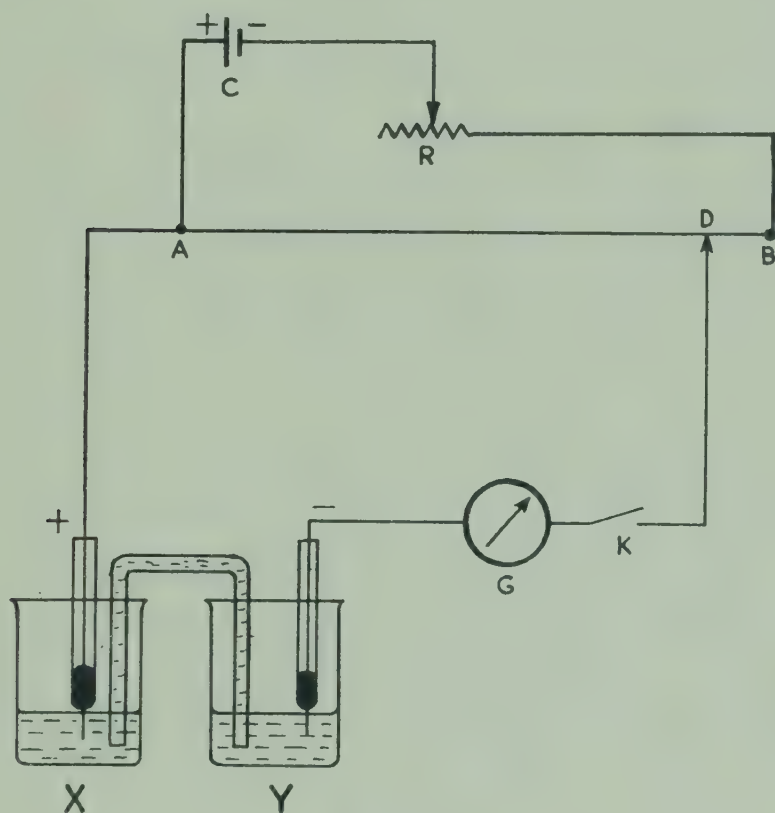


FIG. 37.

stretched over a metre rule (Fig. 37), the ends A and B being connected through a regulating resistance R, with the terminals of an accumulator or good dry cell C. In this way there is produced a regular fall of potential along the wire, and the difference of potential between any two points on the wire A and D will be proportional to the distance between them.

The electrode of the half-cell X containing the acid which is being titrated is joined to the positive (and zero) end A of the potentiometer wire by a direct connection, and the electrode of the half-cell Y of fixed potential is connected through a

sensitive galvanometer G and key K to a contact D which can be moved along the wire. A position is found in which no current flows through the galvanometer when contact is made with the wire, and the length of wire AD intercepted is read. This process is repeated after each addition of the titrating alkaline solution, the connections with the half-cells being reversed when the zero is reached.

When the zero-point has been passed, the lengths recorded may then be graphed against the volume of alkali added up to each point, and the position of maximum slope of the curve found from the graph; or the change in length may be divided in each case by the additional volume of alkali which produced it, and the point of maximum change per unit addition judged from the results.

Exercises (1)—Electrometric Titration of Acid, using Galvanometer only.—Prepare approximately decinormal solutions of sodium hydroxide and hydrochloric acid. Titrate 25 ml. of the acid with the sodium hydroxide, using methyl-orange as indicator.

Pipette 25 ml. of the hydrochloric acid above into a wide 100 ml. beaker, and into a similar beaker put a convenient volume of approximately twentieth-normal sodium chloride solution. Add a little quinhydrone to each, and stir. Immerse in each a platinum electrode, and connect the two vessels with a potassium chloride-agar bridge. Connect up the apparatus through a suitable resistance to a galvanometer, putting a key in the circuit. Arrange the burette containing the sodium hydroxide above, so that this can be run into the acid. Add the alkali at first in quantities of 5 ml., reducing the amount to 2 ml., and finally to single drops as the point of neutralisation previously obtained is approached. After each addition depress the galvanometer key cautiously. When no deflection can be observed in the "acid" direction, take the reading of the burette. Continue to add alkali in drops until a deflection is observed in the opposite or "alkali" direction. Take this reading. The difference between the two readings will show the sensitiveness of the arrangement, and the result should be compared with that obtained by the indicator method.

(2) *Electrometric Titration of Acid, using Potentiometer.*—Connect up the apparatus as shown in Fig. 37, placing 25 ml.

of the hydrochloric acid in the vessel X, and some dilute acetic acid containing sodium acetate in Y. Proceed as in (1) above with the addition of the sodium hydroxide, but now move the contact on the potentiometer wire after each addition to such a position that there is no deflection observable in the galvanometer when contact is made. Record the potentiometer readings and the burette readings in parallel columns. The former may become negative in sign after the neutral point is passed, when the connecting wires to the platinum electrodes must be interchanged. Do not continue the addition of alkali more than 0.2 ml. beyond this point. Plot the results on squared paper, marking off the burette readings horizontally, and the potentiometer readings vertically, the latter being negative after an interchange of connections. Decide by means of a straight-edge the burette reading which corresponds to the steepest slope of the curve through the points recorded.

Calculate also the change in the potentiometer reading *per millilitre added* for each successive addition of alkali. Decide at what reading of the burette this change is greatest. Compare the results with those obtained with methyl orange, and by method (1).

Repeat the above series of experiments, using a decinormal solution of acetic acid instead of the hydrochloric acid. The indicator used for comparison must be phenolphthalein, and in method (1) it is probable that no deflection will be detectable until the point of neutralisation is passed.

By one of the electrical methods above, find the percentage of acetic acid, $CH_3.COOH$ (Eq. Wt. = 60), in a sample of brown vinegar.

THE DETERMINATION OF pH

If the pH of a solution is to be found, the solution must form the liquid of a half-cell with a hydrogen electrode, and be connected by a conducting bridge with another half-cell of known potential. The E.M.F. of the combination is then measured by means of a standardised potentiometer, and the potential of the unknown half-cell deduced. From this the value of the pH of the liquid is obtained by the use of an established formula.

As has been already stated (p. 209), a calomel half-cell is

usually employed as the half-cell of known potential. If the pH of the unknown solution is less than 8, a platinum electrode and quinhydrone are used. If it is greater than 8, an electrode of hydrogen gas must be used, in which case the known half-cell may also consist of a hydrogen gas electrode in a liquid of known pH (Cole, *Practical Physiological Chemistry*).

The Calomel Half-Cell

This is most simply constructed by fitting a small wide-mouthed glass bottle with a rubber stopper bored with two holes, one of the correct width to take a platinum electrode (p. 209), and the other wide enough for a glass tube through which one of the arms of a bridge will pass easily. The lower end of this wide tube should be just below the stopper and the upper end be widened so that it may be closed by a cork when the half-cell is not in use. The platinum electrode is inserted through the stopper so that the end of the wire almost touches the bottom of the bottle. Pure mercury is poured in so that the platinum wire is well covered, even if the bottle is accidentally shaken. Some pure calomel and mercury are rubbed into a paste in a mortar with some of the potassium chloride solution to be used in the cell, and this is then poured onto the mercury. The bottle is then nearly filled with the potassium chloride solution, which should previously have been saturated with calomel. The bridge used to connect this half-cell with that under investigation should have been made with potassium chloride solution of the same strength.

The concentration of the potassium chloride solution used in the calomel half-cell should be saturated, normal, or decinormal, and of these the normal solution is most convenient for ordinary use.

Calculation of pH for the Combination of Quinhydrone and Calomel Half-Cells

For the theory and deduction of the formulæ applying to half-cells, reference must be made to such a book as Grant's *Measurement of Hydrogen Ion Concentration*. When a calomel half-cell made up with normal potassium chloride is used in conjunction with a platinum electrode and quin-

hydron in the liquid under investigation, the pH of this liquid is given by the following formula :—

$$pH = \frac{e_{\text{quin}} - E - e_{\text{cal}}}{0.198T}$$

Where E is the E.M.F. observed in millivolts,

T is the absolute temperature,

e_{quin} is 704.4 mv. at 18°, rising with fall of temperature approximately 0.75 mv. per °C.

e_{cal} is 286.4 mv. at 18°, rising with fall of temperature approximately 0.2 mv. per °C.

The combined value of $e_{\text{quin}} - e_{\text{cal}}$ is 418 mv. at 18° C., rising 0.5 mv. for each fall of 1° C.

Exercise.—Prepare 100 ml. of 0.2N acetic acid and 100 ml. of a 0.2N solution of sodium acetate.

Set up the apparatus as in Fig. 37, and calibrate the potentiometer wire as follows :—In place of the half-cells, connect a standard cadmium cell between the positive end of the potentiometer wire and the galvanometer. Find the balancing point on the wire, and thence calculate the fall in potential in millivolts per centimetre of the wire, taking the E.M.F. of the cadmium cell to be 1018 mv.

The cadmium cell is now replaced by the two combined half-cells, X and Y, the latter being the calomel half-cell. Into a small wide beaker measure from a burette 32.8 ml. of the 0.2N acetic acid and 7.2 ml. of the 0.2N sodium acetate solution. This will give a solution of pH value 4.0. Stir in a little quinhydrone, insert a platinum electrode, and connect with the calomel half-cell by means of an agar bridge of normal potassium chloride. The acetate half-cell X is connected to the positive end of the potentiometer wire. After a minute or so, find the balancing point on the wire, and convert the reading into millivolts.

Calculate the pH of the acetate solution by means of the formula given above.

Repeat the experiment, using a mixture of 12 ml. of 0.2N acetic acid with 28 ml. of 0.2N sodium acetate in the half-cell X. The pH value of this solution is 5.0.

The Hydrogen Electrode

A simple hydrogen electrode may be made as follows :— A platinum wire mounted as described on p. 209 is carefully cleaned, first with fine emery paper, then by immersion for a short while in warm chromic acid mixture (p.58), and finally washed in distilled water. It is then coated all over with a thin coherent layer of platinum black, by making it the cathode in a cell with a platinum anode in a 3 per cent. solution of platinic chloride acidified with hydrochloric acid. As soon as the bright metal is completely hidden by the black deposit, the electrode is washed in distilled water, and the electrolysis continued in a 10 per cent. solution of sulphuric acid. Hydrogen should escape uniformly from the surface. If it does not do so, the wire must be again cleaned, and the process repeated. A prepared electrode must not be allowed to dry, and is stored in distilled water.

The half-cell containing the hydrogen electrode is arranged so that this is immersed in the liquid, and bathed in a continuous current of pure hydrogen, which bubbles past it rapidly until saturation has been attained, and then more slowly. If a cylinder of pure gas is used, it is sufficient to pass the hydrogen through a wash-bottle containing alkaline 2 per cent. potassium permanganate ; but if it is being generated from a Kipp, it should also be passed through a solution of mercuric chloride ; in either case, it is passed finally through a wash-bottle containing the same liquid as that surrounding the electrode.

Determinations of pH by means of the hydrogen electrode are carried out as described in the exercise on p. 215, and the pH is calculated from the formula :

$$pH = \frac{E - e_{cal}}{0.198T}$$

E being the observed E.M.F. in millivolts, and T the absolute temperature. The value of e_{cal} is given on p. 215.

The Glass Electrode

Another form of electrode which offers certain advantages over those considered above is the glass electrode. Its use depends on the fact that a difference of potential exists between a glass surface and a liquid with which it is in contact, the

pH of the liquid determining the magnitude of this difference of potential. The apparatus consists of a thin diaphragm of pure soda-lime glass between two liquids, one of which is of known pH , and the other is the liquid under investigation. Its chief advantages lie in the facts that it is unaffected chemically by the solution whose pH is being determined, and that it can be used for a wide range of pH values. It becomes inaccurate when the pH exceeds 9.5. Special glasses have been developed for use up to pH 13. Its high resistance entails the use of more complicated apparatus than that already described. In conjunction with special thermionic valves, it has largely displaced earlier forms of electrodes for industrial work.

REDUCTION-OXIDATION SYSTEMS

According to the modern view, all reduction-oxidation reactions involve a transfer of electrons, the system which is being reduced gaining electrons, and the system which is being oxidised losing electrons. Thus a change from the ferrous ion to the ferric ion involves the loss of one electron— $Fe^{3+} + e \rightleftharpoons Fe^{2+}$; while the change from the ferricyanide ion to the ferrocyanide ion involves the gain of one electron: $Fe(CN)_6^{3-} + e \rightleftharpoons Fe(CN)_6^{4-}$. In reactions in which iodine is concerned, the oxidation of an iodide ion to free iodine involves the loss of one electron from each iodide ion; and the oxidation of free iodine to a positive iodine ion (as in titrations with potassium iodate in strongly acid solution), involves a further loss of one electron by each atom of iodine:



When an unattackable electrode such as platinum is placed in an oxidising solution, the electrode tends to lose electrons and thereby acquires a positive potential with respect to the solution. This can be measured, and gives an indication of the oxidising tendency of the solution. Such a potential is called the "reduction-oxidation" potential of the solution, or, more briefly, the "redox" potential.

The redox potential, then, is the positive potential acquired by a platinum electrode immersed in the oxidising solution.

This potential only has a definite value where *both* the oxidised and reduced forms of the system are present in

definite amounts. Further, the system must be reversible thermodynamically, that is to say, the application of an infinitesimal potential from an external source must suffice to convert one form of the system into the other. In such a case the redox potential of the system, E , can be expressed by the equation :

$$E = E_o + f \log_e \frac{[\text{oxidised state}]}{[\text{reduced state}]}$$

in which the square brackets represent concentrations or activities, and f is a factor which is constant for the system at any particular temperature. Since the logarithm of unity is zero, it will be seen from this equation that when both oxidised and reduced states are present in equal concentrations, the observed potential is always the same for a given temperature for that system. This potential, represented by E_o in the equation, is called the standard redox potential of the system. The approximate value of E_o in some of the systems made use of in oxidation and reduction processes are given in the table.

Standard Reduction-Oxidation Potentials.

	Volts
Acid permanganate—manganous	1.51
Ceric—cerous (in H_2SO_4 solution)	1.44
Dichromate—chromic	1.33
Ferric—ferrous	0.77
Arsenate—arsenite (in acid solution)	0.56
Iodine—iodide	0.54
Titanic—titanous	0.1
Stannic—stannous	-0.14
Arsenate—arsenite (in alkaline solution)	-0.67

Any system in the table will oxidise one lower in the list, the completeness of the oxidation depending on the difference between the values of E_o for the two systems. Thus in acid solution an arsenate oxidises potassium iodide liberating iodine ; while in a solution made slightly alkaline with sodium bicarbonate the converse reaction takes place, free iodine converting an arsenite almost completely to arsenate.

Reduction-Oxidation Titration by Electrometric Methods

When a system in the reduced state is gradually oxidised its potential will rise, and it will be seen from the equation

given above that this rise will not be regular. As a ratio approaches unity its logarithm changes more slowly, so that if we start with a completely reduced system and gradually oxidise it, the potential at first rises rapidly, and then more slowly. After the mid-point of the conversion the potential again rises slowly at first, and then more rapidly, so that a curve, the centre part of which is flattened, could be drawn. From such a curve, however, the mid-point of the conversion of the reduced system could not be determined accurately.

The approximate position of the end-point of the titration, when the potential has risen to that of the completely oxidised system, can be found by balancing a half-cell containing the liquid which is being titrated against one containing the fully oxidised system, and this method is used in the following exercises.

Exercise (1)—**The Titration of a Ferrous Salt with Potassium Dichromate.**—Prepare approximately decinormal solutions of potassium dichromate and ferrous ammonium sulphate (4.9 and 40 g./l. respectively). Titrate 25 ml. of the ferrous solution with the dichromate, using diphenylamine as an indicator.

Carry out the electrometric titration of further portions of 25 ml. of the ferrous ammonium sulphate in a manner similar to that described on p. 212 (*Exercise 1*), adding dilute sulphuric acid to the ferrous solution, but no quinhydrone. The fixed-potential half-cell should contain a solution of ferric alum acidified with dilute sulphuric acid. The end-point is reached when no movement can be detected in the galvanometer. Compare the result obtained with that given by the titration in which diphenylamine was used as indicator.

Exercise (2)—**The Titration of Potassium Ferrocyanide with Potassium Permanganate.**—Carry out a similar experiment to that above, titrating an approximately decinormal solution of potassium ferrocyanide acidified with dilute sulphuric acid, with decinormal potassium permanganate. The fixed-potential half-cell should contain a solution of the ferricyanide acidified with dilute sulphuric acid.

Difficulty will have been experienced in finding the end-point in the above exercises because of the movement of the galvanometer gradually approaching zero. In the following method

the end-point is more accurately determined by finding the position of a sharp rise in the potential of the titrated mixture. Provided that the oxidising system being added has a standard potential differing sufficiently from that of the system being titrated, a sharp rise in potential will be obtained as soon as the former is present in excess. The position of this rapid rise will therefore mark the end-point of the titration.

Exercises (3) and (4).—Repeat the titrations in Exercises (1) and (2) above, using a method similar to that described under (2) on p. 212. Any fixed-potential half-cell may be employed, and this half-cell is connected to the positive end of the potentiometer wire.

The results of the two electrometric methods may now be compared. Such methods are especially of value where the colour of the liquid prevents the use of any indicator. For example, potassium ferrocyanide may be estimated in the presence of Prussian blue by an electrometric method.

Reduction-Oxidation Titration with the use of Indicators

Those oxidising agents which have themselves a pronounced colour, and which give on reduction a solution which is colourless, serve as indicators in themselves. But in many cases the addition of another substance is necessary for this purpose. Such substances fall into two classes. In one class the indicator is capable of oxidation to a substance of a different colour, the process being irreversible. The use of such an indicator, diphenylamine, has been described under the titration of a ferrous solution by potassium dichromate (p. 134). It is clear that the substance used as an indicator must be less easily oxidised than the substance which is being titrated. In the case of diphenylamine the potential at which a marked colour change occurs is 0.76 volt in acid solution. This is almost identical with that of the standard potential of the ferrous-ferric system. It is therefore necessary, if a satisfactory end-point is to be obtained, to add some substance such as a phosphate or a fluoride to reduce the concentration of the ferric ions by the formation of a complex.

In the other class of indicators are substances which form one side of a reduction-oxidation equilibrium, in which the reduced and oxidised systems have different colours. The laws

which govern the equilibrium in each of these systems are the same as in the case of other reduction-oxidation systems. When present in small amount the indicator system adjusts itself to that ratio between the concentrations of its reduced and oxidised states which corresponds to the potential of the solution in which it is, each such adjustment being accompanied by a change in colour. The most marked change will occur when the potential of the liquid undergoing titration rises rapidly owing to the presence of a slight excess of the titrant, provided that the standard potential of the indicator redox system lies within the range covered by this rapid rise.¹ A difference of 0.1 volt is sufficient to change the indicator system from a point at which 90 per cent. is in the reduced form to one at which 90 per cent. is in the oxidised form, such a change being accompanied by the maximum perceptible alteration in colour.

Many indicators have been found which are suitable for use in reduction-oxidation titrations. As an example, *o*-phenanthroline ferrous sulphate may be cited. This indicator has an intense red colour in the reduced state, and a faint blue colour in the oxidised condition, its standard redox potential being in the region of 1.1 volt. Hence it is suitable for use in the titration of ferrous ions by ceric sulphate or by potassium dichromate, either of which reagents has a standard potential exceeding 1.1 volt, while the standard potential of the ferrous-ferric system is so far below this value that the addition of a substance such as a phosphate to suppress the concentration of the ferric ions is unnecessary. The use of *o*-phenanthroline as an indicator has already been described under the determination of ferrous iron by ceric sulphate, p. 152.

CONDUCTOMETRIC ANALYSIS

The conductivity of a solution of an electrolyte depends not only on the number of ions present in unit volume, but also upon their speed or mobility. Hydrogen ions and hydroxyl ions are by far the most mobile, the mobility of the hydrogen ion being the greater. Other ions, though differing from each other in mobility, do so to a much smaller degree. Hence any

¹ Compare this proviso with that governing the selection of indicators for acidimetry titrations, p. 78.

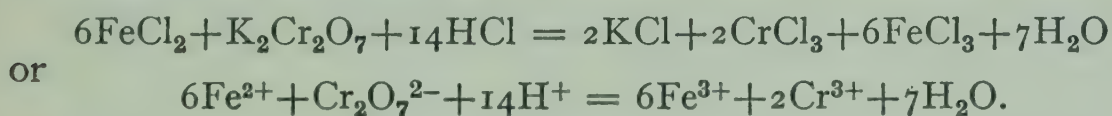
process which diminishes the number of ions present, or substitutes for hydrogen or hydroxyl ions some other ion of lower mobility, lessens the conductivity of the solution and *vice versa*. For analytical purposes it is not usually necessary to determine the specific conductivity of a solution but merely to follow changes in the conductivity as one reactant is added to the other. The method may therefore be applied to neutralisation processes, to certain precipitation processes and even to reduction-oxidation processes if a marked change in the hydrogen ion concentration occurs. It possesses advantages over the ordinary titration methods where the colour of a solution masks that of the indicator, and in some cases gives better results than potentiometric methods. The conductivity method can be used under suitable conditions for titrating very dilute solutions, *e.g.* 0.0001N, and it is practically the only method for the titration of a weak base by a weak acid.

Consider, for example, the titration of a strong acid by means of a strong alkali. The solution at first contains the very mobile hydrogen ion, and therefore the conductivity is high. As the alkali is run in, the added hydroxyl ions combine with the hydrogen ions, which are therefore gradually replaced by the less mobile alkali metal ion, the water formed being practically unionised. The conductivity will therefore become less on this account, even apart from the small increase in the volume of the solution. After the end-point of the titration the additional alkali is no longer neutralised, so that, provided a fairly concentrated solution of alkali is used, there is a rapid increase in the concentration of ions present, one of which is the very mobile hydroxyl ion. The result is a rapid increase in the conductivity of the solution.

If the burette readings obtained in such a titration are plotted against the reciprocal of the resistance of the solution as horizontal and vertical co-ordinates respectively, a V-shaped curve is obtained, and the true end-point can be found from the point of intersection of the two straight lines. A reading need not therefore be made at the end-point; in fact, only three readings before and three after the end-point are necessary, provided that the conditions are so chosen that the readings are represented by two virtually straight lines. This will not be the case if there is a change in the conductivity from a considerable increase in volume on adding the liquid from the

burette. For this reason the normality of the added liquid should be at least ten times that of the liquid being titrated. This involves titrating rather large volumes of liquid if a 50 ml. burette is to be used, but this can be avoided if a micro-burette is available.

There are many applications of the conductometric method in analytical chemistry. In addition to various neutralisation processes it can be applied to precipitation processes, since there is a sudden increase in the conductivity of the solution being titrated after the point of equivalence, as ions are then no longer removed from solution. Therefore, provided that a concentrated solution of the reagent in the burette is used there is a fairly sharp break in the conductivity-volume curve at the point of equivalence. The shape of the curve in this case will be a nearly horizontal line up to the point of equivalence, followed by a line inclining upwards. The conductivity method can also be applied to reduction-oxidation titrations in which hydrogen ions take part, *e.g.* in the oxidation of a ferrous salt by potassium dichromate



The disappearance of the hydrogen ions will cause a fall in the conductivity until the reaction is complete, after which on further addition of potassium dichromate it will remain almost constant.

Since a direct current would electrolyse the solution under investigation, and polarise the electrodes, it is usual to employ an alternating current in conjunction with a Wheatstone bridge. A telephone may be used to determine the balance of the resistances in the bridge, or the alternating current passing through the solution may be rectified by a valve or crystal detector and measured. (For an account of this latter method, see Callan and Horobin, *J. Soc. Chem. Ind.*, 1928, 329 T.) A telephone is used in the apparatus described below.

To obtain accurate results it is necessary to use an alternating current of high frequency, *e.g.* several thousand cycles per second. High-frequency currents can be generated by means of a suitable induction coil, a wireless valve, or other type of oscillator, but it is possible by using a simple "step

down" transformer supplied by current from the A.C. mains (usually 50 cycles per second) to obtain results sufficiently accurate for studying the principles of conductometric analyses. These inexpensive transformers are used for working electric bells or lighting small electric lamps, the output being between about four and eight volts. They possess the advantage over the commonly used induction coil of being almost silent in action.

The telephone to be used for determining the balance of resistance in a Wheatstone bridge (*i.e.* in place of the galvanometer) should have a resistance of between 10 and 30 ohms, the ordinary wireless headphones having far too high a resistance. It is advisable to make one connection of the low voltage A.C. supply to the calibrated wire of the bridge, as

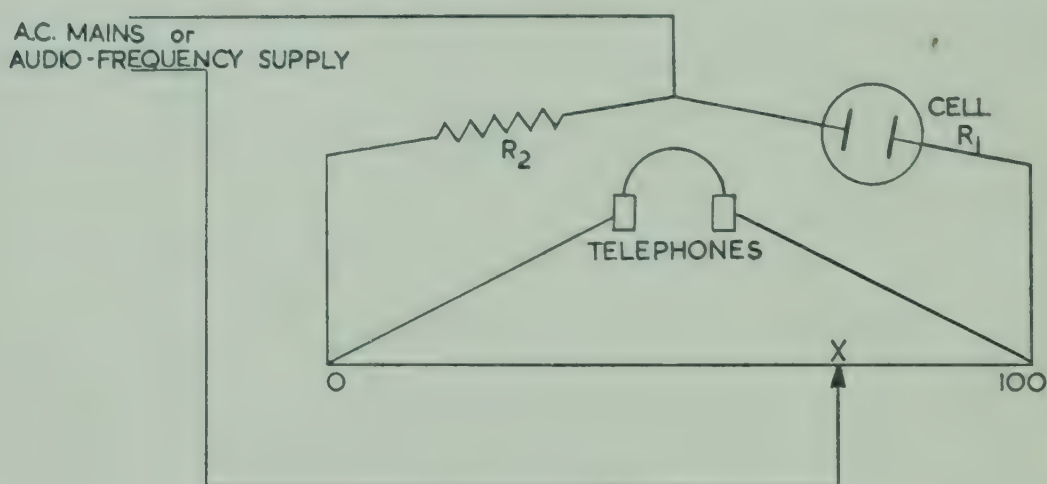


FIG. 38.

this ensures that maximum current passes through the relatively poor contact between the sliding knife-edge and the wire (see Fig. 38).

The conductivity cell can be made from a very wide-mouthed bottle or glass jar of between 75 and 100 ml. capacity, if a 5 ml. micro-burette is available for the titration. If, however, an ordinary 50 ml. burette must be used the cell should have a capacity of 120 to 150 ml. A suitable bung is bored with four holes along a diameter and another hole for a stirrer. The four holes are so placed that by inserting the electrodes in any two of them the distance between the electrodes can be varied to a considerable extent according to the conductivity of the solution being titrated. The two free holes are fitted with a thermometer and the burette to

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be used. The stirrer can be made from a glass rod, onto one end of which is fused a short piece of rod at right angles. The ends of the latter are flattened and bent at an angle to agitate the liquid. The upper end of the rod is connected by means of pressure tubing direct to a small electric motor held in a clamp. The end of the stirrer should almost touch the bottom of the bottle, leaving room for the electrodes to be completely immersed in the liquid above the level of the stirrer vanes. Alternatively, stirring may be effected by means of a current of air. The cell is placed inside a suitable vessel to act as a water-jacket for maintaining the temperature as constant as possible. The electrodes are made of platinum foil (0.15 mm. thick) and to obtain a satisfactory reading of the balance point on the bridge it is necessary to deposit a thin coat of platinum black on both of them, as described below. This reduces polarisation and greatly diminishes noise in the telephone at the balance point. Two pieces of platinum foil about 1 centimetre square each are rubbed with fine emery paper and welded to two pieces of platinum wire 1.5 cm. long and 0.4 mm. in diameter. The welds are easily effected by heating the metal in a blowpipe and hammering the hot wire onto the hot foil resting on an iron block. The free ends of the platinum wires are then fused into glass tubes which will just slide in the holes in the bung, and a little mercury is placed in each tube to make contact with the platinum wire. Before platinum black is deposited on the electrodes, they must be immersed in warm chromic acid mixture (p. 58) for at least ten minutes and then washed in distilled water. Transfer them to a small beaker nearly filled with a solution containing 3 grams of platinic chloride and 10 ml. of dilute hydrochloric acid in 100 ml. of solution. Connect both electrodes to the negative pole of a lead accumulator, and the positive pole of the latter to another piece of platinum foil and immerse this also in the beaker. As soon as the cathodes are completely covered with a black deposit, remove and wash them in distilled water, in which they should be kept until ready for use. When required for use the electrodes should be mounted in the bung so that they are opposite and parallel to each other, and it is important that they should be rigid enough to prevent any relative motion during a titration.

For normal laboratory work it would be better to use an

oscillator or vibrator giving a frequency of a kilocycle or more, since the human ear and the telephone are more sensitive, and polarisation very much less, at such a frequency.

For work of high accuracy it is necessary to use a more refined device. Polarisation may be minimised by using platinised platinum electrodes, and high frequency A.C. current. A conductivity cell has an electrical capacity which should be balanced out by a small variable condenser of, say, $0.00005 \mu\text{F}$ in parallel with the resistance in another arm of the bridge. Non-inductive resistances should be used, and for maximum sensitivity the bridge arms should be approximately equal.

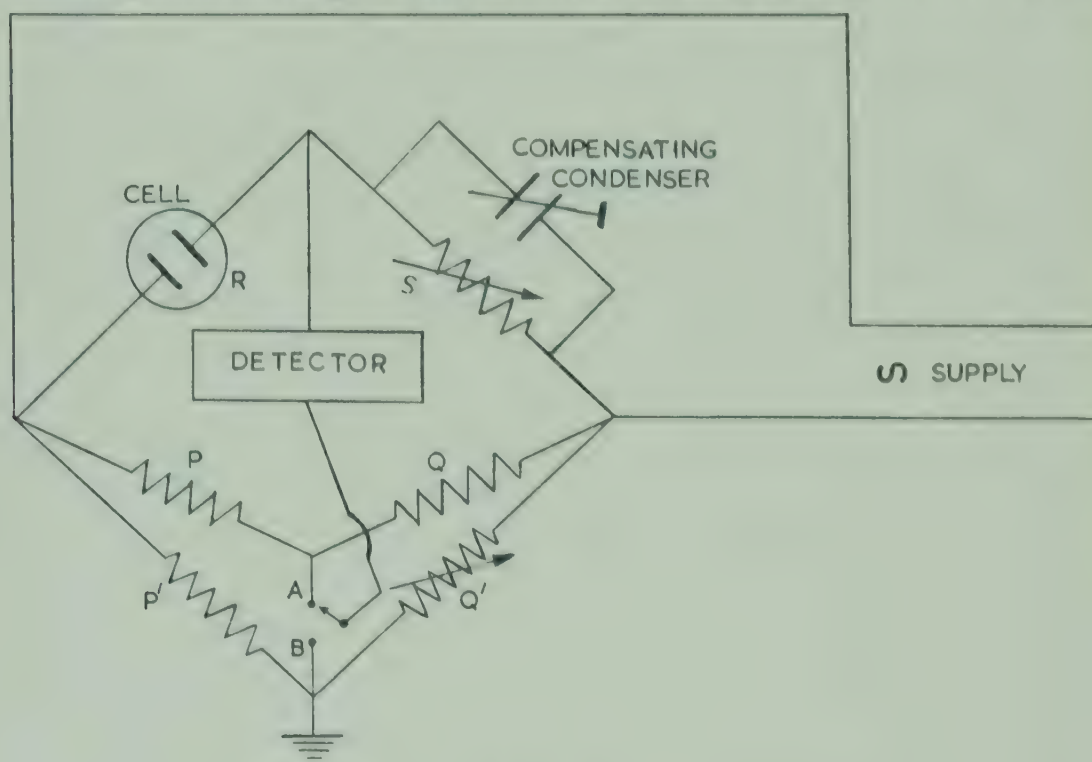


FIG. 39.

For precise silent balance the Wagner earthing system is used ; a telephone earpiece can be used as an extremely sensitive balance detector, but electronic devices are commonly used. The temperature of the cell must be carefully controlled, since some electrolytes have a temperature coefficient of resistance as high as 2 per cent. per $^{\circ}\text{C}$.

A typical circuit incorporating a Wagner earth is shown in Fig. 39. Balance is adjusted with the changeover switch alternately at A and B, which is earthed throughout, until a silent balance at A is achieved, when $R.Q. = S.P.$

Exercise 1.—Titration of Sodium Hydroxide with Hydrochloric Acid—If a 5 ml. micro-burette is available for delivering

the acid, measure 50 ml. of N/100 sodium hydroxide into the smaller cell. If an ordinary 50 ml. burette must be used, measure out 100 ml. of the alkali into the larger cell. Fit the bung carrying the stirrer and the electrodes spaced well apart, since the conductivity in this case will be fairly high. Make sure that the electrodes are completely covered, adding more water if necessary, and insert the thermometer and the tip of the burette containing 0.2N hydrochloric acid through the free holes in the bung. Add water to the outside vessel, which must also be supplied with a thermometer. Run the motor driving the stirrer in the cell slowly and, if necessary, adjust the temperatures of the cell and the jacket to that of the room. Connect the cell to the other components of the Wheatstone bridge as indicated in Fig. 38. About 100 ohms should be a suitable value for the fixed resistance R_2 . Determine the point on the bridge where the sound in the telephone is at a minimum. Make a note of the reading and run in exactly 0.5 ml. of the acid if using a micro-burette, or exactly 1 ml. of acid if using an ordinary burette. When the stirrer has mixed the contents of the cell, again determine the null point on the bridge. The conductivity will be found to have fallen because of the removal of hydroxyl ions. Make further additions of the same volume of acid until at least three readings are obtained after the equivalence point is passed as indicated by a rise in the conductivity because of the presence of the rapidly moving hydrogen ions supplied by the excess of acid. The temperature of the liquid in the cell should not be allowed to rise more than 1° C. (corresponding to a change in the conductivity of about 2 per cent.), the outer jacket being cooled if necessary.

Calculate the value of the resistance of the cell from the equation $R_1 = R_2 \frac{(100-x)}{x}$,

where R_1 = the resistance of the cell,

R_2 = the selected fixed resistance in the bridge,

x = the length of wire between the zero end and the point X, where a balance is obtained.

Plot the reciprocals of R_1 against the volume of acid added, join the points, and determine the point of intersection of the

two lines which gives the volume of the acid equivalent to the alkali taken. Titrate the same volume of alkali, using phenolphthalein as indicator, and compare the result with the conductometric method.

Exercise 2.—Titration of Ammonium Hydroxide by Acetic Acid—This is an instance of the special value of the conductometric method, since the titration of a weak base by a weak acid is not practicable with an indicator, because of the small rate of change in the pH at the stoichiometric point. There is, however, a sufficiently marked break in the conductivity curve to locate this point. If a 5 ml. micro-burette is available, measure out 50 ml. of an approximately $N/50$ ammonium hydroxide solution into the smaller cell and titrate this with an approximately $N/2$ acetic acid solution as described in Exercise 1, or if an ordinary 50 ml. burette is used, take 100 ml. of the ammonium hydroxide. The concentration of the ammonium hydroxide and the acetic acid can be checked by titration with standard hydrochloric acid and sodium hydroxide respectively.

Exercise 3.—Titration of a Ferrous Salt by Potassium Dichromate—For the smaller cell, used in conjunction with a 5 ml. micro-burette, take 50 ml. of approximately $N/10$ ferrous ammonium sulphate made up in $0.7N$ sulphuric acid, or 100 ml. of this solution for the larger cell, and titrate with an almost saturated solution of potassium dichromate.

Exercise 4.—Titration of Sodium Chloride by Silver Nitrate—For the smaller or larger cell take 50 or 100 ml., respectively, of $N/20$ sodium chloride, and titrate with normal silver nitrate.

SUGGESTED READING

- BÖTTGER, W., *Newer Methods of Volumetric Chemical Analysis*, Chapman and Hall, London, 1938.
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PART III

GRAVIMETRIC ANALYSIS

IN gravimetric analysis the final measurement is the determination of weight. The constituent being determined is isolated as a compound of known and definite composition, and the weight of this compound is determined. From the ratio of the weights of the sample and the final product, and from the known relationship between the final compound and the constituent sought, the percentage of constituent present in the sample can be calculated.

Methods of gravimetric analysis can be classified roughly in two groups, evolution methods, and precipitation methods. Of these the second is the more important and the more widely applicable. Evolution methods may be subdivided into those in which the evolved substance is absorbed in some way and weighed, and those in which the loss in weight resulting from the evolution is determined. In the first case it is essential that only the desired substance should be absorbed and weighed. If any other substances are also evolved, then it must be arranged that they do not interfere with the absorption of the substance being determined. This may be done by selecting the absorbent so that unwanted substances are not absorbed, or by first absorbing these substances in a material that will not absorb the compound sought, or by a combination of these methods.

In determinations by loss in weight it is essential that only one substance should be evolved and that the method of evolution should not alter the composition of the material left behind. It is possible, of course, to make corrections for loss in weight caused by evolution of other substances if the amounts of them are known, and corrections can be made for changes in composition of the residue, but such steps naturally cause a greater uncertainty in the results, and it is best to avoid the necessity for them.

Evolution methods are naturally rather limited in scope, and most gravimetric determinations are made by precipitation methods in which the constituent to be determined is isolated

in the form of an insoluble compound which is separated, washed, dried, or ignited to a form suitable for weighing. The precipitation may be brought about by chemical or by physical means. Sometimes, as in cathode electro-deposition methods, the insoluble substance is the element itself.

Although precipitation procedures at first sight seem simple, they are in fact complex, and are liable to error from various sources. First, the precipitate must be insoluble not only under the conditions of precipitation but also in the liquid used to wash it. No compound is completely insoluble, but for practical purposes may be regarded as being so if the amount of it left in solution at the end of the analysis is less than the smallest weight that can be detected on the balance used. Next, the precipitation must be complete; to achieve this it is necessary, though not sufficient, that the precipitant be added in at least slight excess. The precipitate must be free from contamination by other substances and must either be a pure compound of known and definite composition or convertible into such a compound. The compound which is finally weighed, the weighing form, should not be hygroscopic or efflorescent, and should be stable over a fairly wide range of temperature so that precise control of the drying or ignition temperature is not necessary.

The most important source of error, the one that it is hardest to control, is contamination of the precipitate. The ways in which this may arise can be classified in two groups; coprecipitation phenomena and postprecipitation phenomena.

Before the nature of coprecipitation and postprecipitation is discussed it is desirable that precipitation processes in general should be considered. When two solutions which contain between them the ions of an insoluble compound are mixed it would generally be expected that complete and immediate separation of the precipitate would occur. This is, however, by no means always the case, and what happens often depends on the order of addition of reagents. It often happens that a colloidal solution is formed, in which the very finely divided particles of the insoluble substance have acquired an electrical charge, and are thereby kept in suspension. The charge is acquired by the adsorption of anions or cations on the surface of the particles, for every precipitate has a tendency to adsorb its own ions. As might be expected, a secondary adsorption occurs of ions of opposite charge to those primarily adsorbed.

These secondarily adsorbed ions (or counter-ions, as they are sometimes called) cannot approach the surface so closely as the primarily adsorbed ions, but remain a short distance away. In this way the so-called electrical double layer is formed between the particles and the solution. It is this double layer that is responsible for the stability of the colloidal solution. If the double layer is destroyed the particles will coagulate. This can be achieved by addition of a sufficient amount of an electrolyte. The minimum concentration of an electrolyte required to destroy the double layer is called the flocculation value. The flocculation value depends on the charge of the colloidal particles and on the valency and other properties of the ions of opposite charge in the electrolyte. Multivalent ions are much more efficient as flocculants than are univalent ions.

The adsorption effects that occur during flocculation may be quite complicated and will depend, *inter alia*, on the flocculation value of the electrolyte. Usually the ions which determined the charge of the colloid will remain adsorbed after flocculation, together with an adsorption of the counter ions to maintain electrical neutrality. If a strongly flocculating electrolyte has been used, however, there may be replacement of the original counter ions by ions from the flocculant. Obviously, a flocculated colloid will always be contaminated on the surface by adsorption. Washing with water may remove some of the contaminant, but it may also reduce the electrolyte concentration below the flocculation value, with the result that the precipitate may go into colloidal solution again. This effect is called peptisation. It can be avoided by washing the precipitate with a solution of an electrolyte which does not affect the subsequent operations. A solution of an ammonium salt, which can be volatilised in an ignition, may be used, for example.

Flocculated colloids usually age rapidly, especially if they are kept hot, and their surface area is greatly decreased, with a corresponding decrease in the amount of contamination by adsorption. Aging is the term used to describe the changes in the character of a precipitate when it has been allowed to remain in contact with the mother liquor for some time. Usually there is a continuous interchange of the ions of the precipitate between the solution and the precipitate, resulting in a recrystallisation of the precipitate in the form of larger, purer particles. Particles of small size are more soluble than

larger ones, so that in the aging process the larger particles grow at the expense of the smaller ones. If the original precipitate was amorphous (hydrated ferric oxide, for example) the process of aging may lead to the formation of a crystalline form of the precipitate. Unfortunately, it may also make the precipitate more difficult to redissolve if it is desired to reprecipitate it. Hydrated aluminium oxide may be quite insoluble in acids if it has been aged for an appreciable time.

In the case of ionic precipitates, the ions within the body of the crystal will be surrounded by ions of opposite charge, and they will be electrostatically attracted by them in all directions. At the surface, however, there will be a break in the symmetry of the arrangement, and ions in the surface will be able to exert an electrostatic attraction on ions of opposite charge in the solution. This conception largely accounts for the phenomena of coprecipitation and postprecipitation.

Coprecipitation.—This term is applied to the contamination of a precipitate by substances which are normally soluble under the conditions of precipitation. Two main types of coprecipitation may be distinguished ; adsorption at the surface of the precipitate, and occlusion within the precipitate. In the case of adsorption at the surface the degree of contamination is determined by such factors as the nature of the precipitate and the ions present in the solution. Colloidal precipitates adsorb more material than macro-crystalline precipitates do, because they have a greater surface area. Ionic precipitates generally adsorb material in accordance with the Paneth-Fajans-Hahn rule, which states that “ Those ions whose compounds with the oppositely charged constituent of the lattice are slightly soluble in the solution in question are well adsorbed by the ionic lattice.” Silver acetate for example, is more strongly adsorbed than silver nitrate by silver iodide, since the acetate is less soluble than the nitrate. The fact that salts are adsorbed follows from the requirement that electrical neutrality be maintained in the solution. If cations are preferentially adsorbed on the crystal, an equivalent number of anions must also be adsorbed to prevent accumulation of a net positive charge on the precipitate and a negative charge in the solution.

The degree of adsorption also depends on the dissociation constant of the adsorbed compound and on the polarisability of the adsorbed ions. Adsorption generally increases with

decreasing dissociation or with increasing polarisability. Thus hydrogen sulphide, which is a weak electrolyte, is strongly adsorbed by metallic sulphides, and easily polarised anions such as those of certain dyes are readily adsorbed by precipitates. Use of this last fact is made in the use of adsorption indicators in argentometric titrations (see p. 188).

Ionic precipitates may also adsorb ions that are not present in the precipitate. Another possibility is a surface exchange reaction occurring during aging of the precipitate. When a precipitate is allowed to stand in contact with its mother liquor, a continuous process of dissolution and reprecipitation goes on. Finally a kinetic equilibrium is established in which the rate of deposition just equals the rate of dissolution. In the deposition process there may be competition for vacant lattice sites between ions in the solution, leading to a partial replacement of one of the ions in the surface of crystal. There may also be an exchange of counter ions with other ions present in the solution.

Apart from the ionic adsorption mentioned above there may take place adsorption of polar molecules such as water. The dipole of the water molecule is attracted by the ions in the surface of the lattice and is strongly adsorbed.

Occlusion is really a special case of adsorption and it means that ions are adsorbed during growth of the crystals in the precipitate and are trapped within the crystal by the superimposition of further crystal material.

If the occluded material will fit into the crystal lattice of the precipitate it is occluded in the form of mixed crystals or a solid solution. If it does not fit into the crystal lattice it forms the sites of lattice defects. Aging of the precipitate often leads to considerable purification in the second case, but not often in the first.

Postprecipitation.—When this occurs the primary precipitate separates first, and a secondary precipitate of some other slightly soluble substance slowly separates afterwards on the surface of the primary precipitate. The phenomenon usually occurs in the case of those substances which form supersaturated solutions and crystallise slowly. Generally there is a common anion in the primary and secondary precipitates and the phenomenon can be explained in terms of counter ion exchange.

Purification of Precipitates.—From the foregoing it is

evident that precipitates may be purified to some extent by aging and digestion, which promote recrystallisation. By far the best method, however, is reprecipitation, since the amount of contaminant present in the solution will be very much reduced. The degree of purification attained, however, may not always be sufficient. The *relative* amount of adsorption is greater for small than for large concentrations of the contaminant.

NOTES ON APPARATUS

(See also p. 18)

Porcelain Crucibles.—For most ordinary purposes, crucibles of good porcelain, 3 to 4 cm. in diameter, are suitable. Before being exposed to a high temperature, porcelain crucibles should be carefully heated with a small flame in order to avoid fracture. Porcelain crucibles must not be used for substances that are to be treated with hydrofluoric acid, or for fusions with sodium hydroxide, sodium peroxide, or alkali carbonates; and they are not so suitable as platinum crucibles for substances that require heating to a very high temperature. Porcelain crucibles may be permanently marked, for the purpose of identification, by writing in an inorganic ink a distinctive letter on each crucible and lid, drying the ink by gently warming, applying more ink, and finally heating the porcelain to bright redness, so as to burn the residual ferric oxide into the glaze.

Silica Crucibles.—Although probably more fragile than porcelain crucibles, silica crucibles may be safely exposed to sudden changes of temperature without any risk of fracture. Silica vessels must not be used for alkalis or hydrofluoric acid.

Platinum Crucibles.—When the use of a platinum crucible is admissible, it is usually preferable to one of porcelain. Platinum crucibles can be more readily and more uniformly heated to redness than porcelain crucibles. On account of the expense of platinum, however, it is often necessary to restrict the use of platinum vessels to cases where they are indispensable. *The following rules and precautions with regard to platinum vessels must be observed:—*

1. Platinum crucibles must not be exposed to a luminous flame, since this will cause the metal to lose its lustre and to become brittle—probably because of the formation of a carbide of platinum.

2. Compounds of lead, silver, zinc, tin, bismuth, arsenic, and antimony must not be heated in platinum crucibles when there is any possibility of reduction to the metallic state, as the metals, having comparatively low melting-points, may alloy with the platinum.

3. Great care should be taken in igniting phosphates in platinum crucibles, since the presence of reducing substances, such as charred filter paper, may result in the formation of traces of phosphorus which, combining with the platinum, render it brittle. It is safer to use a porcelain crucible for phosphates.

4. Platinum crucibles must not be used for fusions with hydroxides, nitrates, nitrites, and cyanides of the alkalis.

5. Evaporations or fusions in which chlorine, bromine, or iodine is set free must not be performed in platinum vessels. This rule applies to mixtures in which both chloride and nitrate are present: and to ferric chloride in the presence of concentrated hydrochloric acid.

6. Care must be taken to avoid damaging a platinum crucible and causing indentations by dropping it on the bench. It must on no account be squeezed with the object of loosening the solidified cake after a sodium carbonate fusion.

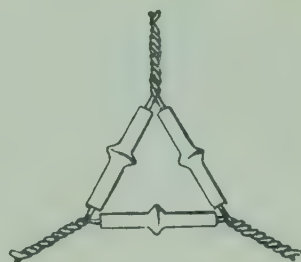


FIG. 40.

7. Platinum ware should be kept scrupulously clean. Adhering substances or stains can sometimes be removed by boiling a little concentrated hydrochloric acid in the crucible, or by fusing a little potassium bisulphate¹ in the crucible and removing the salt by means of boiling water. The crucible should then be polished with fine, moist sea sand, which is gently rubbed on the surface of the metal with the finger. After being polished, the platinum should be rinsed with distilled water and dried.

Triangles.—A very satisfactory form of pipe-clay, silica, or porcelain triangle, on which a crucible is placed during the process of heating, is shown in Fig. 40. For the usual sizes of crucibles, triangles with sides 5 cm. or $6\frac{1}{2}$ cm. long are suitable. Nickel wire is preferable to iron wire on account of

¹ This salt when fused attacks platinum to a slight extent.

its much greater durability. A silica triangle may be used, except with a platinum crucible, to which it tends to adhere because of the reducing action of the flame.

Perforated Silica or Asbestos Screens.—It is often important to exclude flame gases from the interior of a crucible during an ignition, and, for this purpose, the device shown in Fig. 41 may be used. It consists of a silica plate, 13 cm. square, in which is cut a round opening large enough to admit the crucible to two-thirds of its depth. The plate is held in an inclined position by means of a clamp. A higher temperature in the crucible may be reached by using a silica plate with a larger opening, and placing over the latter a disc of platinum in which a hole is cut to fit the crucible. Instead of a silica plate, a sheet of asbestos may be used.

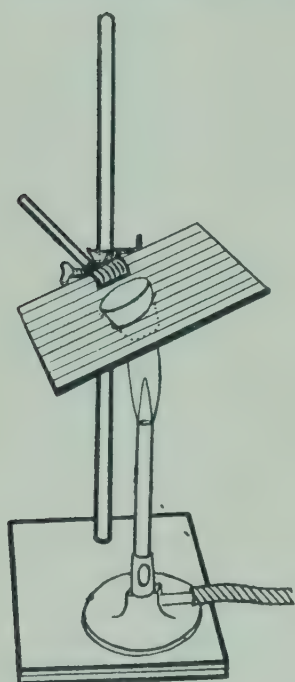


FIG. 41.

Crucible Tongs.—Crucible tongs should be made of brass or of gun-metal, and it is an advantage to have them fitted with platinum tips or the tips covered with thin platinum foil, secured by platinum wire. A useful substitute is a small pair of iron pliers, which may be used to lift a platinum crucible if platinum tipped tongs are not available. All tongs must be kept scrupulously clean.

The Gooch Crucible

Filtration by means of a Gooch crucible is frequently advantageous, and it is a most convenient method of collecting a precipitate directly in the crucible in which it is finally weighed. A porcelain Gooch crucible of the size and shape shown in Fig. 42 is suitable for most purposes. The bottom of the crucible is perforated with a number of small holes. The crucible, which is always used in conjunction with the filter-pump, is fitted into a glass adapter by means of a narrow rubber ring (cut from a piece of rubber tubing, $2\frac{1}{2}$ cm. in diameter), and the adapter passes through the rubber stopper of a filter-flask. The filtering medium must be white, heat-resisting asbestos, and a special kind and quality is sold for the purpose.

Preparation of the Asbestos Filter.—Connect the filter-flask, fitted with the adapter supporting the crucible, to the

filter-pump (Fig. 43). In using a Gooch crucible it is most important that the filtration should not be conducted under too great a pressure, and, to prevent this, the connection with the pump should include some means of regulating the pressure, such as that described on the next page.

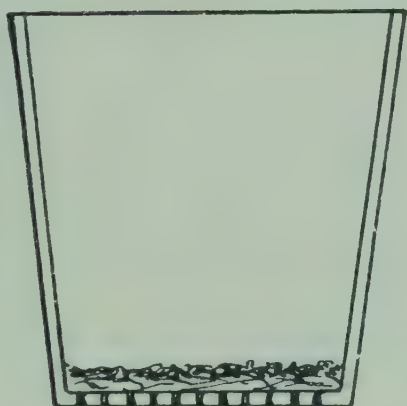


FIG. 42.—Section of Gooch Crucible (Actual Size).

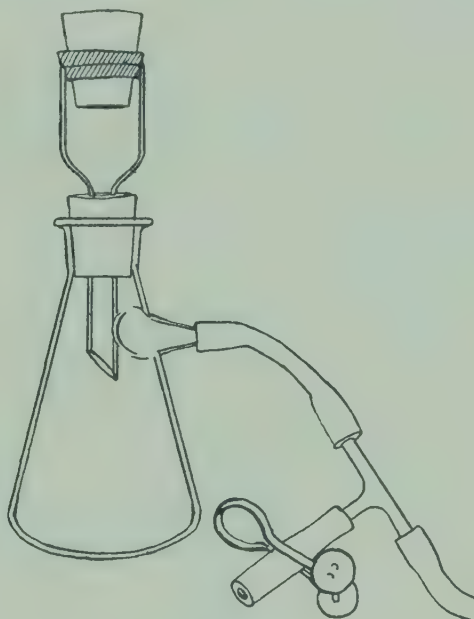


FIG. 43.

Shake about 0.05 gram of the asbestos with 25 ml. of water and pour about 20 ml. of the mixture into the crucible. Allow the water to drain, using very gentle suction. Then turn on the maximum pressure the regulator will allow. Add the remainder of the asbestos and wash the filter with about 100 ml. of warm water. If the filter is properly prepared with suitable asbestos, 100 ml. of water will pass through in about one minute under a pressure equal to that of 5 cm. of mercury.

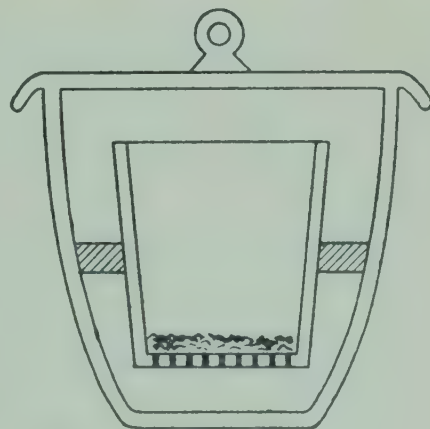


FIG. 44.

Place the crucible on a watch-glass and dry it for an hour in an air-oven at a temperature about 20° higher than that required for the precipitate that is subsequently to be collected in the crucible. If the precipitate requires ignition, place the crucible within a larger platinum or nickel crucible, fitted with an asbestos ring, as shown in Fig. 44, and heat the larger crucible with the flame. Cool the Gooch crucible in a desiccator, and weigh it. It is then ready for use.

It should be borne in mind, when a Gooch crucible is used, that asbestos is hygroscopic.

Pressure Regulator for Use with the Filter-Pump.—

Some means should always be used of limiting the maximum pressure under which filtration by means of the filter-pump is conducted, and the following arrangement is simple and effective.

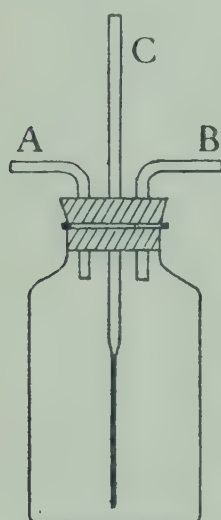


FIG. 45.

Three tubes pass through a rubber stopper fitted into a bottle (Fig. 45). A and B are connected to the filter-pump and to the filter-flask respectively. The tube C is drawn out to form a capillary at its lower end and forms an air-leak. The size (or length) of the capillary is adjusted by trial, so that, when the pump is working at full power, the pressure in the bottle when B is closed cannot fall below a definite value, viz., about 5 cm. of mercury less than atmospheric pressure. The adjustment is easily made with the help of a simple pressure gauge; a piece of glass tubing bent into a U-form and containing mercury is suitable for the purpose.

The bottle also safeguards the contents of the filter-flask from contamination with water from the filter-pump, should the water-pressure momentarily fail. A back rush of water may also be prevented by fitting a suitable ground glass valve between the pump and the filter-flask.

The Sintered Glass Crucible

In this the filtering medium, instead of asbestos fibre, is a fixed layer of sintered glass particles. These crucibles (Fig. 46) can be obtained in widely varying grades of porosity (see Appendix, p. 525). If not used for strongly alkaline liquids, they remain nearly constant in weight for long periods. They can be heated to about 400° in an air-bath. Being ready for immediate use, and of an approximately known weight, they are more convenient than an ordinary Gooch crucible. They are fitted into an adapter in the same manner as a Gooch crucible (see Fig. 43), and used in conjunction with a filter-pump. It has recently been suggested

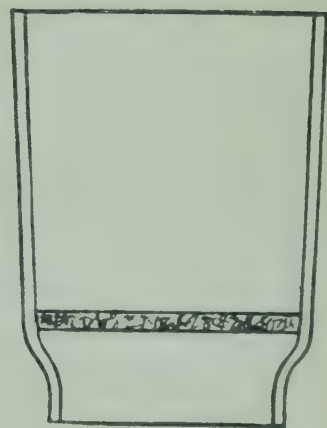


FIG. 46.

that the sintered glass crucible should be ground into the adapter, using corborundum, thus dispensing with the rubber ring.

Similar crucibles made of porcelain or silica, which may be ignited up to 1000° , are now manufactured.

It is convenient to mark the weight of the crucible upon it by etching or with a special ink.

Precipitates may be removed by means of a test-tube brush and water. Particles in the pores of the filter can be dislodged by drawing water through in the reverse direction, or by dissolving the solid in a suitable solvent other than caustic alkali. Concentrated acids may be used without appreciable effect on the filter; acetone is sometimes useful for cleaning and rapid drying. EDTA is particularly useful for removing precipitates such as barium sulphate.

New sintered glass crucibles should always be conditioned before being used in a determination. They should be repeatedly heated with hydrochloric acid, washed, and dried, until weight constancy is attained.

The Rose Crucible

When it is necessary to ignite a precipitate in an atmosphere of hydrogen,¹ carbon dioxide, or oxygen, a Rose crucible is used. The crucible, its cover, and the tube through which the gas is led into the crucible (all of porcelain or silica) are shown in Fig. 47.

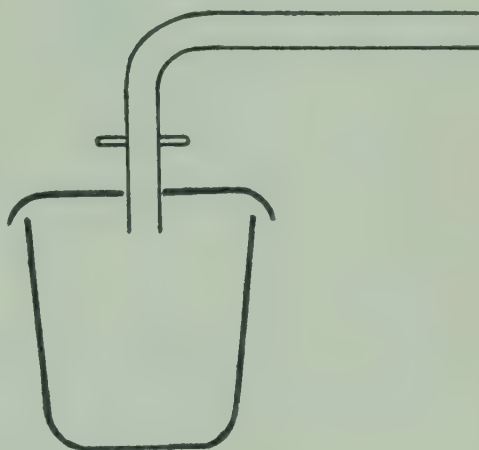


FIG. 47.

THE IGNITION AND WEIGHING OF PRECIPITATES

After a precipitate has been filtered off and washed, it requires further treatment before it can be weighed. In the first place, if a filter paper has been used it must be destroyed by incinerating it either in presence of the whole precipitate or after separating the precipitate from it. The precipitate, together

¹ It is essential before starting the ignition to be sure that the hydrogen is not mixed with air. For the preparation of these gases, see Appendix, p. 515.

with the filter ash, is then "ignited" in a weighed crucible. (The terms "ignite" and "ignition" are commonly used in analytical chemistry, and refer to the process of heating a substance to a high temperature, without allowing the direct access of the flame to the substance.) The purpose of the ignition is (1) to dry or dehydrate the precipitate completely, and, in many cases, (2) to convert the precipitate, which may be of uncertain composition, into another compound of definite and known composition. Copper, for example, may be precipitated as hydrated copper oxide, $\text{CuO} \cdot x\text{H}_2\text{O}$, which is ignited and weighed as anhydrous cupric oxide, CuO ; and zinc may be precipitated as basic carbonate which is of variable



FIG. 48.
Incorrect Position
of Crucible in
Bunsen flame.



FIG. 49.
Correct Position
of Crucible in
Bunsen flame.

composition but it is easily converted by ignition into zinc oxide, ZnO . The weight of the ignited precipitate is then ascertained by weighing the crucible and its contents, and deducting the weight of the crucible and that of the filter ash (unless the latter is negligible) from the total weight.

The ignition is performed by heating the crucible containing the precipitate with the flame of a Bunsen burner, a Méker burner, or a blowpipe, according to the temperature required.

The Bunsen Burner.—A good Bunsen burner, giving a flame of medium size, should be used for heating purposes. In order that it may be possible to obtain suitable non-luminous flames of different sizes, it is most important that the air-regulator of the burner should be in working order; it seldom happens that the mere lighting of the burner, without carefully adjusting the air supply, gives the best flame for a given purpose.

When a Bunsen burner is used for strongly heating a

crucible, rather more air than is just required to produce a non-luminous flame should be admitted by means of the regulator; too much air, however, gives a noisy flame, which is unsuitable. The position of a crucible in a Bunsen flame is important. If the crucible is placed so near the burner that the inner cone of unburnt gas impinges on it (Fig. 48), the bottom of the crucible will not become properly heated. Again, the crucible must not be enveloped in a large flame burning with a restricted air supply. The proper position, in which the bottom of the crucible is about half an inch above the top of the inner cone, is shown diagrammatically in Fig. 49. In order that the position of the crucible in the

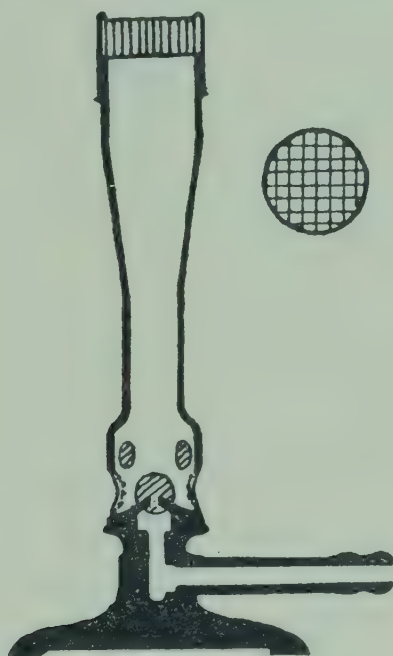


FIG. 50.



FIG. 51.
Correct Position
of Crucible in
Méker flame.

flame may be easily adjusted, the pipe-clay triangle on which the crucible rests should be supported on a movable retort-stand ring.

The Méker Burner.—When a Bunsen flame is fully aerated, the volume of air passing into the burner is about 2.5 times the volume of the gas, whereas for the complete combustion of one volume of coal gas about six volumes of air are required. If a mixture of gas and air in the latter proportions were lighted at an ordinary burner, the flame would “strike back” and burn at the bottom of the tube.

In the Méker burner, the holes for the admission of air are large enough to pass sufficient air for the complete combustion of the gas, and a nickel grid is fitted into the top of the burner

in order to prevent the flame striking back (Fig. 50). The flame of a Méker burner is smaller, and therefore hotter, than a Bunsen flame burning the same amount of gas, and the cold centre of unburnt gas is entirely absent. The hottest part of the flame is close to the nickel grid, but the temperature of the flame is much more uniform than that of a Bunsen flame. For igniting precipitates it is seldom necessary to use a blowpipe if a Méker burner is available.

A special form of the Méker burner—the Amal burner—is equipped with a special regulating device to permit the use of very small flames.

The Muffle Furnace—If many ignitions are to be made it is tedious to use gas burners. It is much more satisfactory to use a muffle furnace heated by gas or electricity. The furnace may be used to do many ignitions simultaneously, and an electrically heated one can be thermostatically controlled so that safe ignition can be made of precipitates which easily decompose if heated at too high a temperature.

Drying the Precipitate and the Filter

It is often necessary to dry the precipitate and the filter before the latter is incinerated. To do this, first remove the water in the stem of the funnel by means of filter paper; cover the mouth of the funnel with a piece of paper, the latter being folded over the rim of the funnel so that each fold overlaps the preceding one; and then place the funnel in the steam-oven in an upright position, and leave it there for several hours until the precipitate and paper are dry.

Incineration of the Filter

In certain cases the filter may be incinerated in presence of the whole precipitate; in others the precipitate must be detached as far as practicable from the filter before the latter is incinerated. The procedure depends on the nature of the precipitate.

The filter must be incinerated apart from the precipitate (1) if the precipitate is fusible or volatile at the temperature of incineration, *e.g.* silver chloride, or (2) if the precipitate suffers reduction to the metallic state during the charring of the filter paper, *e.g.* silver chloride, lead sulphate, zinc carbonate,

or (3) if the compound that is to be weighed is decomposed at the high temperature of the incineration ; *e.g.* if calcium oxalate is to be converted into calcium carbonate, it must not be heated above dull redness.

The filter may be incinerated in presence of the precipitate in the case of (1) silica ; (2) the oxides of iron, aluminium, chromium, and manganese ; and (3) the sulphates of barium, strontium, and calcium.

The incineration is performed in a porcelain crucible, or in a platinum crucible if the use of the latter is permissible (see p. 234).

Generally, if it is inadmissible to ignite a precipitate in the presence of the filter, it is best to use some other means of filtration, such as a sintered glass crucible, or to use a volumetric method.

Tare of the Crucible.—Place the clean crucible, covered with the lid, on a pipe-clay triangle, and heat it to redness for a few minutes with a properly adjusted Bunsen flame. Remove the flame, and after about a minute lift the lid of the crucible with tongs, and place it temporarily on the desiccator cover, which is held inverted in the left hand ; then transfer the crucible and finally the lid to a suitable stand (see p. 20) in the desiccator. (Except on the ground rim, the desiccator cover must, of course, be free from grease.) Allow the desiccator to remain in the balance-room for at least thirty minutes, then weigh the crucible and lid, and afterwards replace them in the desiccator. After the crucible has been heated and weighed it must not be placed directly on the bench, but only on the pipe-clay triangle, in the desiccator, or (when cold) on a sheet of clean paper.

Crucibles must always be ignited to constant weight under the conditions of the final ignition in the experiment before being used for a determination.

Incineration of the Filter in Presence of the Precipitate

When this method is applicable, it is not necessary to dry the precipitate in the steam-oven ; but large precipitates of chromic, ferric, and aluminium hydroxides should be partially dried as described on p. 242, before proceeding with the incineration.

Detach the filter very carefully from the funnel by means of a small spatula and remove it from the funnel. Fold the filter paper so as to form a small packet enclosing the precipitate, taking care not to tear the paper. Place the packet in the weighed crucible and press it down gently. Remove any trace of the precipitate adhering to the funnel with a piece of "ashless" filter paper—first moistening the funnel, if necessary, by breathing into it—and drop this piece also into the crucible. Place the crucible on a pipe-clay triangle in a slanting position and cover it partially with the lid, which should rest

partly on the triangle, as shown in Fig. 52.

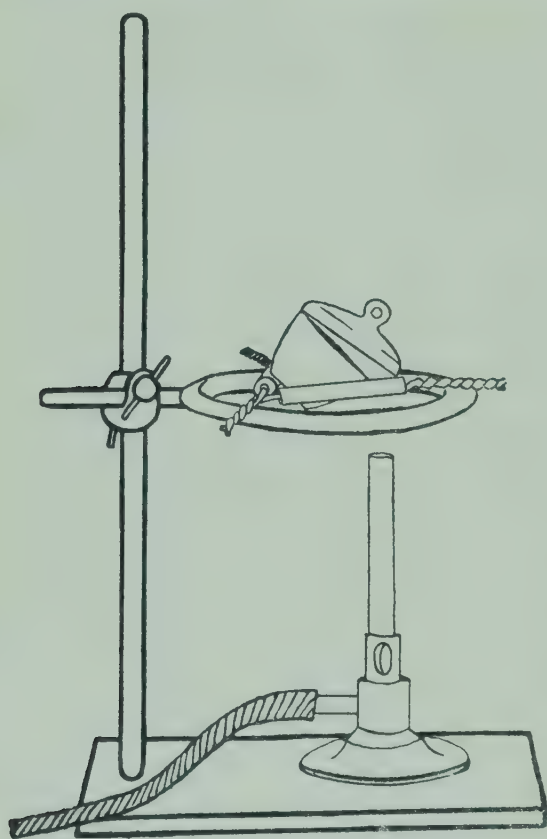


FIG. 52.

Place a small (2 cm.) flame under the crucible lid and about $2\frac{1}{2}$ cm. from it, as shown in the figure. The hot gases are deflected into the crucible, and the contents soon become dry. When the paper begins to char, remove the lid of the crucible and place it meanwhile on a glazed tile or a watch-glass. Place the crucible upright, and adjust the size of the flame and the distance of the crucible from it, so that the paper gradually chars without taking fire. If the paper should take fire, remove the flame and cover the crucible with the lid for a moment. When the escape of

vapour ceases and the charring of the paper is complete, place the crucible *in a sloping position* again and heat more strongly until all the carbon is oxidised. If the carbon burns with difficulty, the oxidation may be accelerated by shifting the crucible into various sloping positions, so that all parts that are blackened with carbon may become properly heated. A deposit of carbon is sometimes found on the under surface of the crucible lid, but this is easily removed by heating the inverted lid with the flame.

The precipitate is now ready for ignition, and the special instructions given for each should be followed. After igniting, remove the flame, wait for about a minute, then place the crucible

in a desiccator and allow it to cool for at least thirty minutes. Weigh the crucible with its contents.

The ignition must be repeated as often as may be necessary until constant weight is attained. By "constant weight" is here meant that the difference between two consecutive weights is not more than two-tenths of a milligram, *i.e.* 0.0002 gram. The weighing must be performed as quickly as possible, especially if the precipitate is hygroscopic, and, when a weighing is repeated, all the weights used in the previous weighing should be placed on the balance before the crucible is removed from the desiccator. It is a mistake to leave an ignited precipitate in a desiccator for a long time, *e.g.* overnight, before weighing it; it should be re-ignited, and then weighed after cooling for thirty minutes.

Incineration of the Filter apart from the Precipitate

The precipitate and filter must be dried as far as possible in the steam-oven. Two sheets (about 25 cm. square) of glazed paper¹—white if the precipitate is coloured, and black if the precipitate is white—are laid on the bench. A shallow porcelain basin, about 5 cm. in diameter, or a watch-glass of the same size, is placed on one of the sheets. The Bunsen burner or other metal apparatus, from which particles of rust or dirt are liable to drop, must not on any account be placed on the glazed paper.

Remove the well-dried filter from the funnel. Hold the filter over the glazed paper and loosen the precipitate by gently pressing the cone-shaped filter with the fingers. Transfer the bulk of the precipitate very carefully to the basin or watch-glass. Carefully unfold the filter and loosen the precipitate still adhering to it by lightly rubbing with the paper itself, care being taken, however, not to rub off any paper fluff. Empty this portion of the precipitate into the basin, then place the latter on the second sheet of paper, and cover the basin meanwhile with a clock-glass.

Fold the filter paper into a narrow strip, as shown in A to D (Fig. 53), the shaded portion in A representing the soiled part of the paper, which is inside after folding as in B. Carefully wipe off any traces of the precipitate adhering to the

¹ The glazed paper must have clean-cut edges and be free from creases, and should be kept flat and unfolded between two pieces of cardboard.

funnel by means of the paper strip—first breathing into the funnel in order to moisten it—and then wrap up the strip into a compact roll, as shown in E and F. Place the roll in the weighed crucible which, meanwhile, is left in the desiccator.

If any precipitate has been allowed to fall on the glazed paper, transfer it very carefully to the basin by bending, but not folding, the sheet, and sweeping the particles into the basin by means of a small brush.

Now place the open crucible containing the filter on a pipe-clay triangle, and incinerate the filter in the manner described on p. 244. Allow the crucible to cool, and then

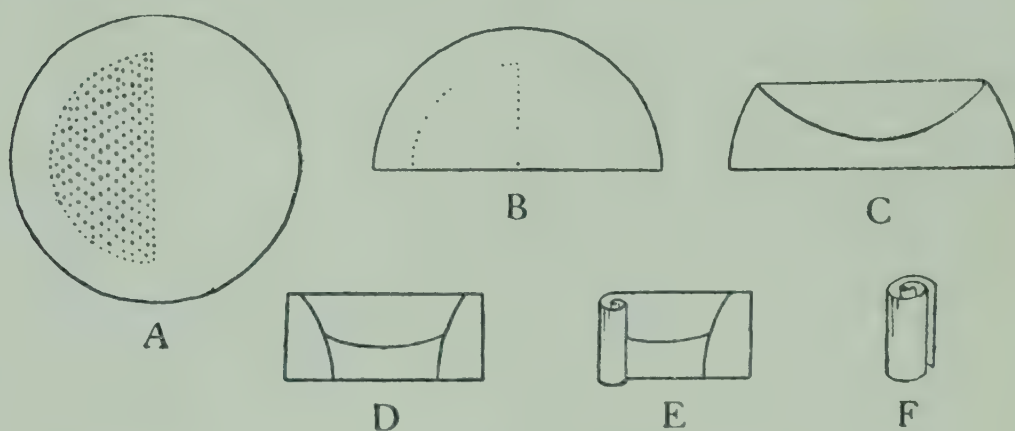


FIG. 53.

treat the filter ash in accordance with the instructions given for the particular precipitate (see, for example, silver chloride or copper oxide). When the crucible is cold again, place it on the glazed paper, and very carefully transfer the main part of the precipitate to the crucible. Finally, dry or ignite the precipitate in the manner specified, and repeat the process until constant weight is attained.

Weighing Precipitates without Ignition

(I) **Use of Tared Filter Paper.**—Occasionally it is necessary to weigh on the filter paper a precipitate which would be decomposed by ignition, and for which a Gooch or sintered glass crucible would not be suitable. In such a case the paper before use is folded as usual for insertion in a funnel, the apex then doubled back, and the paper rolled into cylindrical form. This is then placed in a weighing-bottle, and dried at 105° —

not in a steam-oven ¹—until constant in weight. After filtration and washing, the filter is first dried in the funnel in a steam-oven, then transferred to the weighing-bottle, and the drying completed at 105°.

(2) **Use of Acetone in Drying Precipitates.**—In certain cases, when the composition of the precipitate after simple drying is known, ignition may be avoided and the time of procedure much shortened, by using a Gooch or sintered glass crucible, and, after washing the precipitate as directed to get rid of the salts in solution, continuing the washing with acetone. The precipitate and the inside walls of the crucible are well rinsed about five times with 5 ml. portions of acetone, air drawn through the filter for a few minutes, and the drying finished in a vacuum exsiccator, or by placing for a few minutes in a steam-oven, or low temperature air-oven. Among the precipitates suitable for this treatment are barium sulphate, mercuric sulphide, the halides of silver, lead sulphate, calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), and magnesium ammonium phosphate ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$).

¹ Filter paper retains some moisture if heated in an ordinary steam-oven, the temperature of which is below 100°. Air-ovens which are thermostatically controlled are useful for many drying operations.

Typical Gravimetric Exercises

THE following section contains a number of simple exercises which have been so selected that they involve all the more important manipulative operations of gravimetric analysis. Each exercise can be performed with a salt which is readily obtainable in a state of purity, and the experimental result can therefore be checked by calculation. It may be preferred, however, to perform the analyses with solutions or solids of "unknown" composition. A list of solutions that are suitable for this purpose, with particulars as to their preparation, is given in the Appendix.

Most of the exercises given in this section should be carried out before the analyses described in later sections of the book are attempted. The exercises are arranged roughly in order of difficulty, except that, for convenience in description, the determination of aluminium has been placed immediately after that of iron, although it presents more difficulty than many of the other exercises.

Determination of Water in Magnesium Sulphate Heptahydrate

OUTLINE OF METHOD.—A weighed quantity of the magnesium sulphate is heated to dull redness, and the loss of weight, which represents the water, is ascertained.

Procedure.—Heat a crucible and lid with a full Bunsen flame for five minutes. Remove the flame, allow the crucible to cool for about a minute, and then place it in a desiccator for half an hour. Weigh the crucible and lid accurately. Place about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, in the crucible, and weigh again. Place the covered crucible resting on a pipe-clay triangle, about 15 cm. above a small flame (not more than $2\frac{1}{2}$ cm. high). At intervals of a few minutes, lower the crucible and increase the flame gradually until the bottom of the crucible is heated to dull redness. Maintain the crucible at this temperature for about ten minutes.

Allow the crucible to cool in a desiccator for half an hour, and weigh. Repeat the heating process until constant weight is attained.

From the loss of weight, calculate the percentage of water in magnesium sulphate heptahydrate.

Determination of Water in Barium Chloride Crystals

Weigh accurately in a tared porcelain crucible 1.5 to 2.0 grams of barium chloride crystals, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Heat the crucible and contents to a temperature *not exceeding dull redness* until constant weight is attained (compare previous exercise). From the loss of weight, calculate the percentage of water in the barium chloride crystals.

Determination of Anhydrous Disodium Hydrogen Phosphate in the Crystalline Salt

In a tared porcelain crucible weigh accurately about 0.5 gram of sodium phosphate, $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (selected crystals free from efflorescence). Heat the crucible and contents for about an hour in the steam-oven, and then at a gradually increasing temperature with a Bunsen flame. Finally, ignite at a red heat for about ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained. The residue is sodium pyrophosphate,



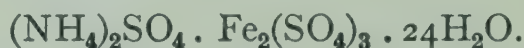
From the weight of sodium pyrophosphate obtained, calculate the percentage of anhydrous disodium hydrogen phosphate in the original crystals.

Determination of the Iron in Ammonium Iron Alum

OUTLINE OF METHOD.—The salt is converted into ferric oxide by heating in a crucible, and the percentage of iron in the alum is calculated from the weight of the oxide obtained.

This method of determining iron is applicable only to compounds that leave a residue, after ignition, consisting of pure ferric oxide. It cannot be used, therefore, for salts that contain a non-volatile impurity.

Procedure.—Weigh accurately in a tared crucible about 1.5 gram of ammonium iron alum,



Heat the covered crucible and contents very gently over a small flame; gradually increase the temperature until full redness is attained, and then continue the ignition with a Méker burner for fifteen minutes. Cool for one minute, transfer to the desiccator for about thirty minutes, and weigh. Repeat the ignition and weighing until the weight is constant.

The result of the experiment should be recorded as follows:—

Weight of crucible and alum	10.6842 g.
Tare of crucible and lid (1st ignition)	9.1722 g.
" " " (2nd ")	9.1722 g.
Weight of alum taken	1.5120 g.
Weight of crucible and Fe_2O_3 (1st ignition)	9.4241 g.
" " " (2nd ")	9.4234 g.
" " " (3rd ")	9.4234 g.
Weight of Fe_2O_3 obtained	0.2512 g.

159.7 grams Fe_2O_3 represent 111.7 grams Fe, and the percentage of iron in the alum is therefore

$$\frac{0.2512 \times 111.7 \times 100}{159.7 \times 1.5120} = 11.61$$

Percentage of iron required by the formula = 11.58
Difference = +0.03

The error is 3 in 1158, or +0.26 per cent. This corresponds to 0.6 mg. of ferric oxide.

Other Examples of Analysis by Ignition

Many other determinations may be carried out in the manner described in the last exercise. The method is easier and more expeditious than a precipitation method, but it is applicable only if the residue left after ignition is a pure substance, such as a pure oxide.

The residue left on ignition is usually an oxide. Before proceeding to the analysis, study the properties of the oxide

in order to ascertain to what extent it may safely be heated ; as a rule, this information may be obtained by reference to Part V. of this book.

The following are typical cases in which this method may be used :—

Barium in barium peroxide and nitrate. The residue left after ignition is barium oxide, BaO .

Bismuth in bismuth oxynitrate and carbonate. The residue left after ignition is bismuth oxide, Bi_2O_3 .

Calcium in calcium acetate, hydroxide, carbonate, and nitrate. The residue left after ignition is calcium oxide, CaO .

Copper in copper hydroxide, carbonate, and nitrate. The residue left after ignition is cupric oxide, CuO .

Lead in lead hydroxide, peroxide, carbonate, and nitrate. The residue left after ignition is lead monoxide, PbO .

Zinc in basic carbonate. The residue left after ignition is zinc oxide, ZnO .

It is often possible, by slight modification of the procedure, to apply this method to other salts, *e.g.*—

- (1) The iron in ferrous ammonium sulphate may be determined by oxidation of a weighed sample with concentrated nitric acid and subsequent ignition. The residue obtained is ferric oxide.
- (2) Some sulphates are completely converted into oxides by repeated ignition, with addition of a few small pieces of solid ammonium carbonate before each ignition.

Determination of Iron as Ferric Oxide

OUTLINE OF METHOD.—The iron, after oxidation to the ferric state if this should be necessary, is precipitated as hydrous ferric oxide by adding ammonia. The precipitate is filtered and washed. The filter is incinerated together with the precipitate, and the latter is converted into ferric oxide and weighed as Fe_2O_3 .

Hydrous Ferric Oxide is a reddish-brown, flocculent precipitate, practically insoluble in water, in dilute alkalis, and in ammonium salts, but readily soluble in acids. It is often called ferric hydroxide. In order to obtain it free from basic salt it should be precipitated by adding a moderate *excess* of ammonia to a cold or warm (but not boiling) solution, the latter

being continuously stirred. If washed free from the last trace of soluble salts, ferric hydroxide occasionally passes through the filter in the form of a brown colloidal solution. This can be prevented by washing the precipitate with a 2 per cent. solution of ammonium nitrate (*not* chloride) instead of with water.

Ferric Oxide, obtained by heating the hydrated compound, is reddish-brown or almost black in colour, according to the temperature of the ignition. Contact with a reducing flame converts it partially into Fe_3O_4 , or even into metallic iron. If ferric oxide is ignited with ammonium chloride, a little ferric chloride volatilises. The ignited oxide dissolves very slowly in concentrated hydrochloric acid.

Exercise.—Weigh accurately, in a scoop or watch-glass, about 1.3 gram of ammonium ferric sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ (ammonium iron alum). Transfer it to a 400 ml. resistance-glass beaker, provided with a suitable clock-glass and stirring-rod (see Fig. 8, p. 34). Dissolve the salt in water, add 5 ml. of dilute sulphuric acid, and determine the iron as follows.

Procedure.—Dilute to about 150 ml., warm the solution and precipitate the iron by adding a moderate excess of dilute ammonia (15 to 20 ml.), the solution meanwhile being continuously stirred. For very accurate work, the ammonia should be freshly prepared by dissolution of the gas. Leave the stirring-rod in the beaker, cover the beaker with the clock-glass, and heat the contents until boiling. Boil for about one minute, and make sure that ammonia is present in the escaping steam. Remove the flame, place the beaker on a paper mat, rinse the underside of the clock-glass into the beaker with hot water, and allow the precipitate to settle.

Before beginning to filter the precipitate, read the general instructions regarding the filtration and washing of precipitates given on pp. 39 to 44.

Fit a 7-cm. funnel with an 11-cm. paper. For this precipitate the type of funnel shown in Fig. 19 on p. 45 and the open-texture variety of filter paper (p. 40, footnote) are preferable.

Begin the filtration by decanting as much as possible of the clear liquid into the filter without disturbing the precipitate; pour the liquid down the stirring-rod, the latter being held against the beaker, and direct the liquid against the side of the filter and not into the apex (Fig. 15, p. 40). Do not fill the

filter paper quite to the brim. Replace the beaker on the paper mat, add about 80 ml. of hot water—pour the water against the side of the beaker in order to avoid loss by splashing—and stir well. Allow the precipitate to settle, and once more decant the clear liquid into the filter. Repeat this process three times.

Now transfer the precipitate to the filter by pouring as much of it as possible down the rod into the latter, and, by means of a jet of hot water, washing the remainder into the filter in the manner described on p. 43. Remove any traces of precipitate adhering to the beaker and stirring-rod by rubbing with another stirring-rod tipped with rubber tubing, and rinsing. This treatment should be repeated several times.

Any precipitate that cannot be removed in this way must be dissolved in dilute nitric acid (2 to 3 drops mixed with 1 ml. of hot water), which is brought into contact with the entire surface of the beaker by means of the stirring-rod; a few drops of ammonia are then added in order to reprecipitate the ferric hydroxide, and the minute precipitate is collected in a separate *small* filter which is then carefully washed.

Finally, carefully scrutinise the beaker in a good light in order to make sure that no trace of precipitate remains. A small piece of moistened filter paper should be rubbed round the inside of the beaker, and if any stain is visible on this, the paper should be added to the precipitate. Both stirring-rods should be similarly treated.

The precipitate and filter paper must now be thoroughly washed in the following manner:—(1) Direct a fine stream of hot water against the filter paper—blowing gently at first in order that the impact of the water-jet will not cause a portion of the precipitate to be projected out of the funnel—and then, with a rotary motion of the wash-bottle jet, wash the precipitate as far as possible into the lower part of the filter. Allow the filter to drain completely, and repeat. (2) Direct the water-jet round the margin of the filter paper—which must be washed with great care—and then into the mass of the precipitate, which should be well churned up in the operation. Allow to drain, and repeat the washing until the filtrate is found to be free from sulphate, using for the later stages a hot 2 per cent. solution of ammonium nitrate in order to prevent the formation of a sol of ferric hydroxide which would pass through the

filter. In order to test for sulphate, rinse the end of the funnel-stem with water, and then collect about 1 ml. of the filtrate in a test-tube; add a few drops of barium chloride solution, and warm. When no turbidity is observed, the washing is complete.

While the filtration is in progress, a clean crucible (porcelain or platinum) is ignited at a red heat, cooled in a desiccator for thirty minutes, and weighed. The ignition is repeated until constant weight is attained. The filter, together with the precipitate, is then incinerated without previous drying, in the manner described on p. 244. When the incineration is complete, ignite the ferric oxide with a full Bunsen flame in the partially covered crucible for ten minutes, cool in a desiccator for thirty minutes, and weigh. Repeat the ignition until constant weight is attained.

If a Bunsen flame only is used, slightly high results are always obtained for iron, presumably because of retention of traces of moisture (*cf.* aluminium oxide, below). Ignition for 15 minutes with a Méker or Amal burner causes appreciable loss of weight in a precipitate which has been ignited to constant weight with a Bunsen flame. There is no danger of conversion to magnetic oxide when ferric oxide is heated with these burners.

From the weight of Fe_2O_3 obtained, calculate the percentage of iron in ammonium iron alum.

Determination of Aluminium as Oxide

OUTLINE OF METHOD.—The aluminium is precipitated as aluminium hydroxide by means of ammonia in presence of ammonium chloride. The precipitate is converted into the oxide by ignition, and it is weighed as Al_2O_3 .

Aluminium Hydroxide is a bulky, gelatinous precipitate, slightly soluble in ammonia, but almost insoluble in ammonia containing ammonium salts. Freshly precipitated aluminium hydroxide dissolves readily in dilute acids, but after keeping for some time it becomes almost insoluble. It is easily peptised. It is converted into alumina by ignition; a very high temperature is required for complete dehydration.

Aluminium Oxide (Alumina), obtained from the hydroxide by ignition, dissolves very slowly in hot concentrated hydrochloric acid. It may be brought into solution easily after fusion with potassium pyrosulphate. It is not decomposed or volatilised at the highest temperature attainable with a blowpipe flame.

Exercise.—Weigh accurately, in a scoop or a watch-glass, about 1.4 gram of ammonium aluminium alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$. Transfer it to a 400 ml. beaker provided with a clock-glass cover and stirring-rod. Dissolve it in water, and determine the aluminium as follows.

Procedure.—Dilute the solution to about 100 ml. and add 10 ml. of concentrated hydrochloric acid and 40 ml. of dilute ammonia, which, for accurate work, should be freshly prepared by dissolution of the gas. Heat until almost boiling, add 1 ml. of methyl red indicator followed by dilute ammonia, drop by drop, until the solution becomes distinctly yellow (avoid excess). Boil for two minutes. Filter, and wash the precipitate in the same manner as described for ferric hydroxide (p. 252), using a hot 2 per cent. solution of ammonium nitrate instead of hot water throughout, to prevent peptisation.

Dry the precipitate (partially at least) in the steam-oven. Incinerate the filter in presence of the precipitate in a weighed platinum crucible (p. 244), and finally ignite for ten minutes with a Méker burner or a blowpipe, preferably in a crucible furnace to attain a higher temperature. Cool over concentrated sulphuric acid in a desiccator, and weigh. Repeat the ignition until constant weight is attained.

Calculate the percentage of aluminium in the ammonium aluminium alum. Record all weighings, and state the error of the result in the same way as shown on p. 250.

Determination of Chloride as Silver Chloride

OUTLINE OF METHOD.—The chloride is precipitated as silver chloride by the addition of silver nitrate. The precipitate is filtered off in the usual way, and, after incineration of the filter, is weighed as AgCl ; or, preferably, the precipitate is collected and weighed in a Gooch or sintered glass crucible.

Silver Chloride is not quite insoluble in water. At 18° , 1 litre of water dissolves 1.5 mg. It is much more soluble in hot water, 1 litre of which, at 100° , dissolves nearly 22 mg.; for this reason, a silver chloride precipitate must be washed with *cold water*. The solubility in very dilute hydrochloric and nitric acids and in dilute silver nitrate solution is very small; on the other hand, silver chloride is decidedly soluble in concentrated hydrochloric acid and in concentrated solutions

of silver nitrate and most chlorides (1 litre of saturated sodium chloride solution dissolves 1 gram of silver chloride).

On exposure to sunlight, silver chloride loses chlorine, becoming first violet and then nearly black and although this change is at first superficial, the loss of weight is appreciable. Silver chloride melts at about 455° and volatilises appreciably.

Exercise.—Weigh accurately about 0.4 gram of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. Transfer it to a 300 ml. beaker, dissolve it in water, and determine the chloride as follows.

Procedure.—Dilute the solution to about 100 ml., and add 5 ml. of dilute nitric acid. To the cold solution add silver nitrate solution gradually, while stirring briskly, until precipitation of the chloride is complete. A large excess of silver nitrate must not be added and is easily avoided, since the precipitate coagulates as soon as a small excess of silver nitrate is present. In order to protect the silver chloride from bright light, wrap a piece of brown paper round the beaker, using a rubber band to fix the paper in place. Place the beaker on the steam-bath, and stir the liquid frequently until the precipitate has completely coagulated and the liquid is perfectly clear. Make certain that precipitation is complete by adding another drop of silver nitrate, and then allow the solution to cool.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate several times by decantation with cold water containing a few drops of nitric acid. (The nitric acid prevents the silver chloride becoming colloidal and passing through the filter.) Transfer the precipitate to the filter in the usual way, and wash with cold water acidified with nitric acid, until a portion of the filtrate gives no turbidity with dilute hydrochloric acid. Finally, wash with pure water until the filtrate is free from acid (test with litmus paper). Dry the precipitate in the steam-oven.

Incinerate the filter, apart from the precipitate, in a porcelain crucible in the manner described on p. 245. The carbon should be burned at as low a temperature as possible. By means of a glass rod, add 2 drops of concentrated nitric acid to the ash in the crucible and warm gently; then add 1 drop of concentrated hydrochloric acid and cautiously evaporate to dryness. (The object of this procedure is to convert into silver chloride the metallic silver produced during the incineration of the filter.) Transfer the precipitate to the crucible, and either heat the

open crucible for five minutes with a very small flame, great care being taken not to fuse the precipitate, or dry the precipitate in the air-oven at 130° for an hour. Cool, and weigh.

A more convenient method of filtering off silver chloride is by means of a Gooch crucible with an asbestos filter (p. 236), or a sintered glass crucible (p. 238). The crucible is dried in the air-oven at 130° and weighed. After collection and washing of the precipitate in the crucible the latter is heated for an hour in the oven at 130° , and is then cooled and weighed.

From the weight of silver chloride obtained, calculate the percentage of chloride in the barium chloride.

Determination of Copper as Cupric Oxide

OUTLINE OF METHOD.—The copper is precipitated as hydrated copper oxide by means of sodium hydroxide. The filter is incinerated apart from the precipitate, and the latter is converted into cupric oxide by ignition, and is weighed as CuO .

Copper Hydroxide, precipitated from a cold solution, is a light blue substance which becomes dark brown or black when boiled with the alkaline solution. The change in colour arises from loss of water, the composition of the black precipitate being probably $3\text{CuO} \cdot \text{H}_2\text{O}$. The precipitate is slightly soluble in sodium hydroxide solution, and readily soluble in ammonia and in dilute acids. Precipitation is incomplete in presence of organic matter or ammonium salts.

Cupric Oxide, produced from the hydrated oxide by ignition, is a black, hygroscopic powder, which remains unaltered at a red heat, provided reducing gases are carefully excluded.

Exercise.—Weigh accurately about 0.8 gram of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. Transfer it to a 400 ml. Pyrex beaker or a large casserole, dissolve it in water, and determine the copper as follows.

Procedure.—Dilute the solution to about 150 ml. and heat until almost boiling. Remove the flame, add 1 ml. of phenolphthalein, and drop in from a burette, while stirring, a dilute solution of pure sodium hydroxide until the supernatant liquid is definitely pink. A *large* excess of alkali must be carefully avoided. Boil the contents of the covered vessel for about one minute, and then allow the precipitate to subside.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate several times with hot water by decantation.

Transfer the precipitate to the filter. Wash the precipitate and the filter—especially the margin of the latter—until a portion of the filtrate gives no turbidity on boiling with 1 drop of dilute hydrochloric acid and 1 ml. of barium chloride solution.

It frequently happens that a small quantity of the copper oxide adheres to the side of the beaker and cannot be detached by rubbing with a rubber-tipped stirring-rod. In order to remove it, add 2 drops of dilute nitric acid, and bring the acid into contact with the entire surface of the beaker by means of the stirring-rod; rinse down the interior of the beaker with a very little hot water, heat the solution to the boiling-point over a minute flame, and reprecipitate the copper oxide by adding a few drops of sodium hydroxide (avoid excess). Transfer the minute precipitate at once to a separate *small* filter, and wash thoroughly.

Dry both filters very thoroughly in the steam-oven. Incinerate the filters, the larger one apart from the precipitate, in a weighed porcelain crucible in the manner described on p. 245. When all the carbon is burned, allow the crucible to cool and moisten the ash with 2 drops of concentrated nitric acid in order to oxidise any reduced oxide formed during the incineration. Heat the crucible very gently with a minute flame until fuming ceases, and then heat to dull redness for about a minute. When the crucible has become nearly cold again, place it on glazed paper, and carefully transfer the main precipitate to the crucible.

Heat the copper oxide in the open crucible to dull redness for five minutes, cool in a desiccator as usual, and weigh. Repeat the ignition until constant weight is attained. During the ignition every care must be taken that reducing gases are excluded from the interior of the crucible, and for this purpose a perforated silica plate or asbestos board (p. 236), instead of a pipe-clay triangle, should be used to support the crucible.

From the weight of the copper oxide obtained, calculate the percentage of copper in the copper sulphate.

Determination of Zinc as Oxide

OUTLINE OF METHOD.—The zinc is precipitated as basic carbonate by means of sodium carbonate. The filter is incinerated apart from the precipitate, and the latter is converted into zinc oxide by ignition, and is weighed as ZnO .

Basic Zinc Carbonate, the composition of which varies according to the conditions of precipitation, is a white powder,

very slightly soluble in water, and readily soluble in acids, alkali hydroxides, and ammonia. It is slightly soluble in sodium carbonate, and excess of the reagent must therefore be avoided. If the zinc solution contains much sulphate, sodium carbonate always precipitates some basic sulphate, and the precipitate, after filtration, must be dissolved again and reprecipitated; with a small amount of sulphate this is unnecessary. The basic carbonate is converted into zinc oxide by ignition.

Zinc Oxide is yellow when hot, but almost white when cold. It may be heated to bright redness without volatilisation, but if carbonaceous matter, such as traces of filter paper, is present, partial reduction to metallic zinc occurs, and the zinc volatilises readily.

Exercise.—Weigh accurately about 0.8 gram of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 300 ml. Pyrex beaker or casserole, dissolve it in water, and determine the zinc as follows.

Procedure.—Dilute to about 100 ml., and to the cold solution add sodium carbonate (not ammonium carbonate) solution drop by drop until a faint turbidity appears; then heat until boiling. In this way the greater part of the zinc is precipitated as basic carbonate free from alkali carbonate. Now add 1 ml. of phenolphthalein and more sodium carbonate until the solution becomes distinctly pink. Boil for several minutes.

After the precipitate has settled, decant the clear liquid through a 9-cm. filter, and wash the precipitate three times with hot water by decantation. Transfer the precipitate to the filter, and continue the washing until a portion of the filtrate gives no turbidity with hydrochloric acid and barium chloride (p. 258).

Dry the precipitate and the filter in the steam-oven. Separate the precipitate as completely as possible from the filter, without, however, rubbing off any paper fluff, and wrap up the paper in the manner described on p. 245. In order to prevent as far as possible the reduction of any zinc carbonate still adhering to the filter paper, moisten the paper with a few drops of ammonium nitrate solution, and dry it in the steam-oven for a few minutes. Incinerate the paper in a weighed porcelain crucible at as low a temperature as possible. When all the

carbon is burned, add the precipitate, and heat the crucible gently at first, and then to bright redness for ten minutes. Use a good oxidising flame and take care to exclude flame gases during the ignition, otherwise reduction of the oxide and loss of zinc (by volatilisation) will occur. Cool, and weigh. Repeat the ignition until constant weight is attained.

From the weight of zinc oxide obtained, calculate the percentage of zinc in zinc sulphate.

Note.—In order to avoid the risk of loss during the incineration of the filter, the zinc carbonate may be filtered off by means of a Gooch crucible (see p. 236). The crucible containing the precipitate is dried in the steam-oven or air-oven, and is then placed in a larger nickel crucible, or small tin on the bottom of which is a thin sheet of asbestos, and ignited with a full Bunsen flame.

Determination of Sulphate as Barium Sulphate

OUTLINE OF METHOD.—The sulphate is precipitated as barium sulphate by the addition of barium chloride, and the precipitate, after ignition, or drying in a sintered glass crucible, is weighed as BaSO_4 .

Barium Sulphate, obtained by precipitation, is a fine, white powder which is not quite insoluble in water. At 18° , 1 litre of water dissolves 2.3 mg. It is from twenty to thirty times more soluble in cold dilute (normal) hydrochloric and nitric acids. It dissolves freely in concentrated sulphuric acid, but is reprecipitated on diluting the acid. In dilute sulphuric acid and in barium chloride solution it is practically insoluble. Pure barium sulphate may be ignited in air at a red heat without alteration of weight.

The marked tendency of barium sulphate to carry down traces of other substances contained in the solution is a common source of error in the determination of sulphate. The co-precipitated substances cannot always be removed by washing or ignition, and the results are accordingly high; sometimes an impure precipitate decomposes slightly on ignition, and low results may be obtained. In order to reduce the error to a minimum, and to obtain a granular precipitate suitable for filtration, the following conditions must be observed:—

1. The solution must be free from iron (ferric), aluminium, chromium, nitrate, and chlorate. The metals can be

removed by precipitation with ammonia ; nitrate and chlorate by repeated evaporation with concentrated hydrochloric acid.

2. The solution should contain a little hydrochloric acid (about 2 per cent. by volume of the dilute acid), and its volume should not be less than 250 ml. for each 0.5 gram of barium sulphate.
3. The barium chloride solution should be dilute (about 3 per cent.), and may be acidified with a few drops of dilute hydrochloric acid.
4. Precipitation must take place slowly, the hot barium chloride solution being added drop by drop to the nearly boiling sulphate solution, and an excess (about 5 ml.) of the barium chloride should be introduced after the precipitation is complete.¹

Exercise.—Weigh accurately about 0.6 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. Transfer it to a 400 ml. beaker, dissolve in water, and determine the sulphate as follows.

Procedure.—Dilute the solution to about 250 ml., add 5 ml. of dilute hydrochloric acid, and heat until boiling. Prepare an approximately 3 per cent. solution of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), acidify about 30 ml. of the solution with a few drops of dilute hydrochloric acid, and heat until boiling. Lower the flame under the magnesium sulphate solution until the latter just ceases to boil, rinse the cover-glass into the beaker, and add the *hot* barium chloride solution drop by drop²; stir constantly while precipitation is in progress.

When the precipitation appears to be complete, allow the precipitate to settle, and ascertain whether the addition of a

¹ If the barium chloride is added rapidly, the precipitate will contain an appreciable amount of chloride. After precipitation is complete, however, an excess of barium chloride may safely be added, in order to diminish the solubility of the barium sulphate.

² A simple form of dropping-tube, by means of which the barium chloride (or other reagent) can be added slowly, is made by drawing out a test-tube in the blowpipe flame so as to form a capillary through which the solution will pass at the rate of about 2 drops per second. The tube, charged with the hot barium chloride solution, is supported over the beaker in a clean clamp. A funnel attached by rubber tubing to a glass tube drawn out to a capillary may be used instead.

few more drops of barium chloride produces any further precipitate. If no turbidity appears immediately, make sure that there is none after waiting for a minute. (In order to avoid incomplete precipitation, particular care is necessary at this stage, since the precipitation of barium sulphate from a dilute solution is not visible immediately the reagent is added.) After all the sulphate is precipitated, add an additional 5 ml. of barium chloride solution, stir briskly, and then set the beaker aside for about an hour.

Decant the clear liquid through a 9-cm. filter, and wash the precipitate twice with hot water (by decantation). Transfer the precipitate to the filter. Wash the precipitate and the filter with hot water, until a portion of the filtrate gives no turbidity with a few drops of silver nitrate.

After drying, incinerate the filter in a weighed crucible in the manner described on p. 244. After all the carbon is burned, allow the crucible to cool. In order to convert into sulphate any sulphide that may have been formed during the burning of the filter paper, add 2 or 3 drops of a mixture consisting of 1 ml. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised, and then ignite with a full Bunsen flame for ten minutes. Cool, and weigh. Repeat the ignition until constant weight is attained.

The filtration, drying, and weighing may more conveniently be carried out in a Gooch or sintered glass crucible, as described under the determination of chloride (p. 255).

From the weight of barium sulphate obtained, calculate the percentage of sulphate (SO_4^{2-}) in the magnesium sulphate.

Determination of Calcium as Oxalate

OUTLINE OF METHOD.—The calcium is precipitated as calcium oxalate by means of ammonium oxalate, and the precipitate is either weighed as the monohydrate, or is converted into and weighed as CaO or CaSO_4 , or is ignited and weighed as CaCO_3 .

Calcium Oxalate, $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, is a fine, white powder which is very slightly soluble in water. At 18° , 1 litre of water dissolves about 6 mg. It is more soluble in hot water; at 95° , 1 litre of water dissolves about 14 mg. It is somewhat less soluble in dilute ammonia than in water. It dissolves easily in hydrochloric and nitric acids, but very sparingly in acetic

acid. It is somewhat soluble in magnesium chloride solution. Dried at 100° , the precipitate has the composition of the monohydrate; if heated to a temperature approaching dull redness, it is converted into calcium carbonate.

Calcium Carbonate may be heated to about 500° without appreciable decomposition. The dissociation pressure increases (slowly at first and then rapidly) with the temperature, and if the carbonate is heated above 800° in a vessel from which the carbon dioxide can escape, it is completely converted into calcium oxide.

Calcium Oxide is a hygroscopic substance, and should be exposed to the air as little as possible during weighing. As it also absorbs carbon dioxide readily, it should be kept in a desiccator containing soda-lime or sticks of sodium hydroxide.

Calcium Sulphate remains unaltered at a dull red heat. Slow decomposition, with loss of sulphur trioxide, occurs at bright redness.

Exercise.—Weigh accurately 0.4 to 0.5 gram of powdered calcite (calc spar). Transfer it to a 400 ml. beaker. Add about 10 ml. of water, cover the beaker with a clock-glass, and dissolve the calcite by adding dilute hydrochloric acid (about 10 ml.). Dilute with a little water, and boil the solution for a few minutes in order to free it from carbon dioxide.

In the procedure described below it will be observed that the precipitation of the calcium oxalate is begun in a weakly acid solution, and completed in a solution made slightly alkaline with ammonia. This treatment produces a precipitate which is easily filtered for reasons which are discussed on p. 38.

Procedure.—Add a few drops of methyl red, and carefully neutralise the solution with ammonia. Then add 5 ml. of dilute hydrochloric acid, dilute the solution to about 200 ml., and heat until boiling. While continuously stirring, add gradually a moderate excess (35 to 45 ml.) of a hot 2 per cent. solution of ammonium oxalate (freshly prepared). Complete the precipitation by adding ammonia drop by drop until the solution is alkaline, boil for a few minutes, care being taken, by stirring, to avoid bumping, and set the beaker aside for one hour.

Filter through a 9-cm. paper, and wash the precipitate three times by decantation with cold, dilute ammonia (25 ml. of 2N ammonia diluted to 100 ml.). Transfer the precipitate to the

filter, and continue the washing, preferably with a saturated solution of calcium oxalate, until a portion of the filtrate gives no turbidity with nitric acid and silver nitrate.

(1) *If the precipitate is to be weighed as the monohydrate of calcium oxalate*, it must be filtered in a Gooch or sintered glass crucible, and washed as described above. Finally, it is washed either with three small portions of alcohol followed by similar treatment with ether, or with five small portions of acetone. In either case the crucible is then placed in an oven at 80° to 100° for half an hour, cooled, and weighed.

(2) *If the precipitate is to be converted into and weighed as calcium oxide*, incinerate the filter, together with the still moist precipitate, in a weighed *platinum* crucible, in the manner described on p. 244. After all the carbon is burned, heat the crucible, gently at first, and then with a Méker burner for twenty minutes. Cool over concentrated sulphuric acid in a desiccator, and weigh. Repeat the ignition (for ten minutes) until constant weight is attained.

(3) *If the precipitate is to be weighed as calcium sulphate*, a porcelain or silica crucible may be used. Proceed as in (2), but ignite with a Méker burner for five minutes only. Cool, and then slake the calcium oxide by pouring about 1 ml. of water into the crucible. (The water must be added all at once, not drop by drop.) Then add an excess (about 10 drops) of concentrated sulphuric acid. Heat the crucible in an air-bath (Fig. 44, p. 237), gently at first and then with a full Bunsen flame, until the excess of sulphuric acid has been volatilised. Ignite the dry sulphate at low redness, cool, and weigh. Repeat the treatment with acid (add a few drops only), etc., until constant weight is attained.

(4) *If the precipitate is to be weighed as calcium carbonate*, collect it in a sintered porcelain crucible, dry it in an air-oven, and then ignite it to constant weight in an electric muffle furnace at a controlled temperature of 500° .

Electrolytic Methods

ELECTROLYTIC methods are confined almost entirely to the determination of metallic radicals and, as a rule, the metal is deposited as such on the cathode. In the case of lead, it is found better so to adjust the conditions of electrolysis that the lead is deposited as lead dioxide on the anode. If a metal is to be determined electrolytically it must (1) be deposited in a pure state; (2) be deposited completely from the solution; and (3) form a coherent deposit on the electrode. Sometimes electrolytic methods are used to separate metal ions. In this case a mercury cathode is used, and the deposited metals form an amalgam with the mercury.

The nature of the deposit and the accuracy of the determination depend on a number of conditions, among which are the rate of deposition, the composition of the solution, and the temperature. The correct conditions vary for different metals and must be adjusted for each metal within fairly narrow limits. Important factors are potential difference, current density, temperature, hydrogen ion concentration, and composition of the electrolyte. Current density is the amount of current, measured in amperes, per 100 sq. cm. of cathode surface immersed in the solution. Thus, if a current of 1.5 amperes is used and the area of cathode immersed is 75 sq. cm., the current density is $1.5 \div 0.75 = 2$ amps./100 sq. cm.

For occasional analyses in which speed is not essential, stationary electrodes may be employed. A platinum dish, crucible, or stout wire can be used as the cathode, if specially designed electrodes are not available. For routine analyses, where speed is essential, it is necessary to use a stirrer or rotating electrode in order to keep that portion of the electrolyte which is in close proximity to the electrodes in rapid circulation. Otherwise the high current density which is of necessity being used causes liberation of hydrogen on the cathode, preventing the deposited metal from adhering satisfactorily. The conditions for rapid movement of the electrolyte are attained by the use of electrodes such as those designed by Sand (see p. 268).

To obtain the high current density required to effect a reasonably rapid deposition, the resistance of the electrolyte must be kept as low as possible. The type of Sand's electrodes which consists of two concentric wire gauze cylinders satisfies this condition, since the distance between them is only of the order of 3 millimetres.

Separations.—It is often possible to separate metals and estimate them quantitatively by electrolytic means, making use of the difference between their deposition potentials. As an illustration of this the estimation of copper and nickel in a mixture of their sulphates may be cited. To the solution a potential difference of not more than 2 volts is applied, and the current noted. So long as any copper remains, the voltage at the electrodes will vary but little, and no nickel will be deposited. After all the copper has been removed, however, a sharp rise in the voltage will be required to maintain the current density. The cathode may now be weighed to determine the copper, and the nickel then deposited, using a higher voltage.

A more satisfactory method depends on the result of altering the hydrogen ion concentration of the electrolyte considerably between the deposition of the two metals. An example of this method is given on p. 274.

Composition of the Solution.—Sulphates and nitrates are often the best electrolytes, but it is sometimes necessary to use solutions containing complex salts, such as "double" oxalates, tartrates, or cyanides, in order to obtain satisfactory and complete deposition of the metal. The concentration of acid present is often an important condition, especially in securing the separation of metals. The presence of hydrochloric acid, or of a chloride in an acid solution, must be avoided, since the chlorine discharged at the anode will attack the platinum. If chloride is present, it should be expelled by evaporating the solution with concentrated sulphuric acid.

Source of Current.—By far the most satisfactory source of current for this work is a battery of lead accumulators capable of giving up to 5 amperes at an E.M.F. of 2 to 10 volts. The specific gravity of the acid must be tested from time to time. It is not advisable to run an accumulator after the voltage has fallen below 1.9 volts, or the specific gravity below about 1.1.

Stationary Electrodes.—For some purposes, a platinum

basin holding about 150 ml. of liquid is a convenient cathode. The inner surface should be roughened (suitable basins with the surface roughened by a sand-blast may be purchased) in order that the deposit may adhere firmly. This roughened surface must never be cleaned with sand or other abrasive material. As anode, a stout perforated platinum disc, shaped like a saucer (Fig. 54), may be used, or a stout platinum wire may be wound in a flat spiral as shown in Fig. 55. The stout platinum wire D is used to clamp the electrode in position and to make the electrical connection.

It is sometimes inconvenient to use a platinum basin to contain the electrolyte and to serve as cathode, *e.g.* in case it is necessary to remove the electrolyte and wash the deposit without interrupting the current (see p. 270). Instead of the basin electrode, the cathode may take the form of a cylinder of platinum gauze which is suspended, together with the anode, in a beaker containing the electrolyte. When the deposition is complete it is easy, with this arrangement, to remove the cathode and simultaneously to rinse it with water—without previously interrupting the current; or, instead, the beaker containing the electrolyte may be removed and another beaker, containing water, immediately substituted.



FIG. 54.



FIG. 55.

A stand with insulation between the positive and negative terminals is convenient for use with a basin electrode, the basin being supported on a conducting plate; if a special stand is not available, the necessary insulation may be obtained by clamping the anode support D in a rubber cork, and fitting a terminal to the upper end.

Rotating Electrodes.—Rotating electrodes for use in rapid determinations have been designed by Sand. In one form, the cathode (Fig. 56), consists of a stationary platinum wire gauze cylinder attached by stout platinum wires to a split collar at the top. A glass tube with an expanded upper end slides tightly through this collar, and separates the two electrodes. The anode (Fig. 57) consists of a platinum wire gauze

cylinder of smaller diameter than the cathode, and is attached to a platinum-iridium tube of such a diameter that it will just fit inside the glass tube, but rotate freely within it. When the apparatus is set up, there is a clearance of only some 3 mm. between the inner and outer cylinders, so that the resistance of the electrolyte between them is very low. In another form

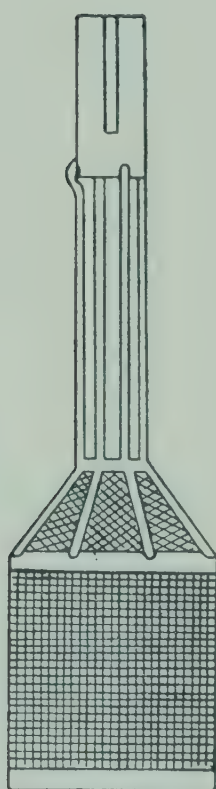


FIG. 56.

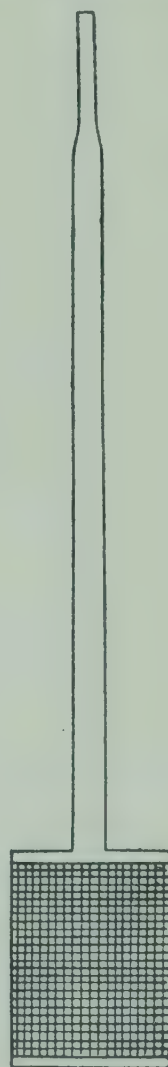


FIG. 57.

the rotating anode has inside it a platinum partition designed to stir the liquid more effectively.

The platinum-iridium tube of the anode is gripped by a small chuck attached to a vertical spindle or shaft supported by a suitable bearing, and carrying a pulley at the top. Power from an electric motor is supplied to the pulley by belt drive, electrical contact with the rotating anode being made through the bearing, or, better, by means of a cup containing mercury at the top of the pulley. This latter method is essential if voltage measurements are to be made. Connection with the

cathode is made by a suitable clamp with a platinum-foil lining to prevent abrasion.

Sand later designed electrodes which require much less platinum for their construction. They consist of quartz glass frames on which is supported platinum wire gauze. The weight of platinum required is about 7 grams for the outer, and 4 grams for the inner electrode.

Sand's electrodes are now not much used. Instead, it is customary to have concentric gauze electrodes supported by a

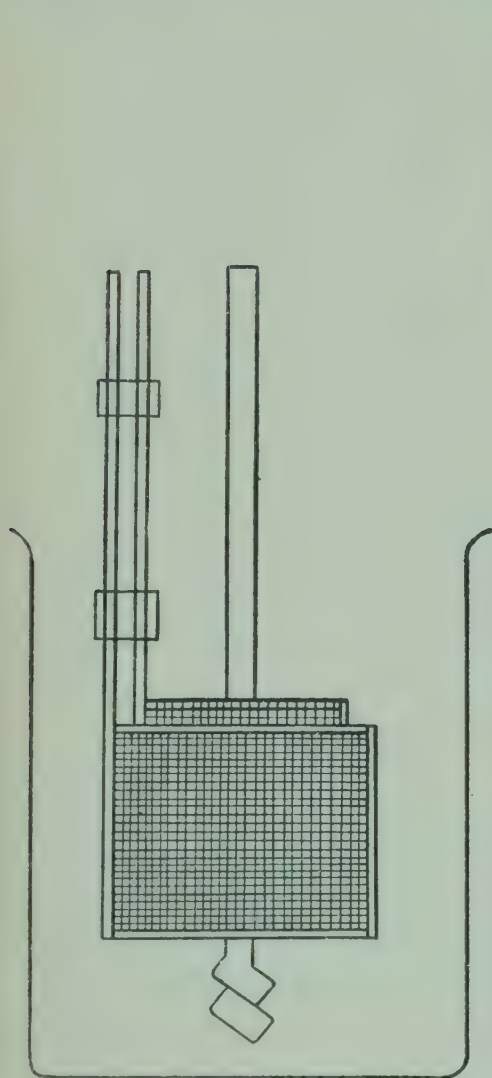


FIG. 58a.

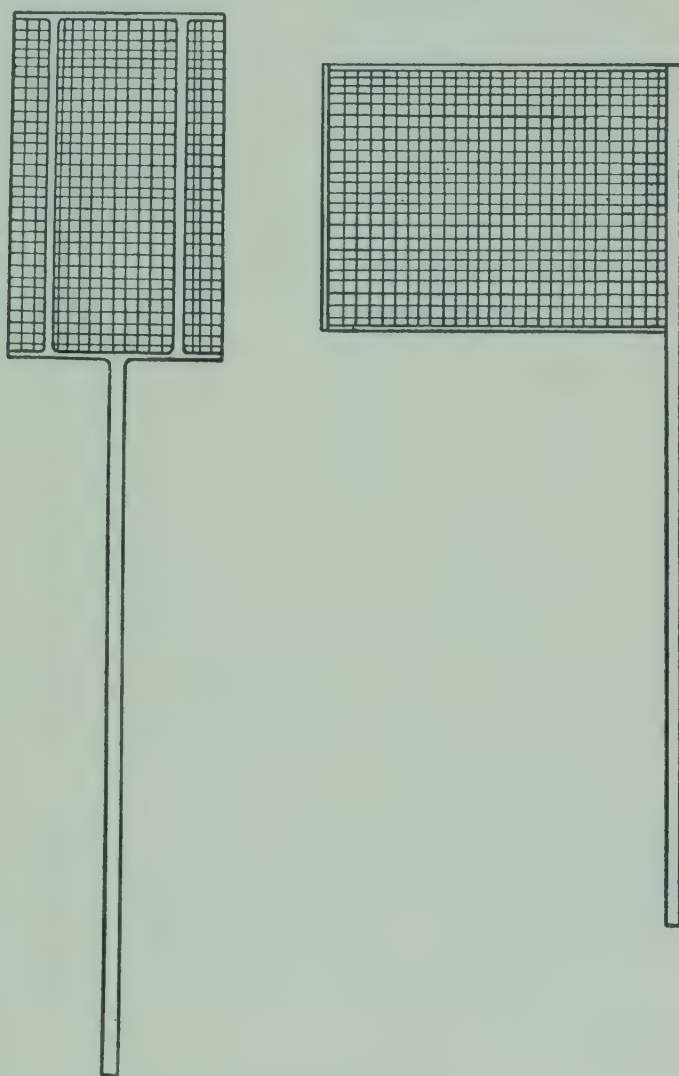


FIG. 58b.

stout wire attached to the side, and to stir the solution with a mechanical stirrer (Fig. 58a). Sometimes a stationary cathode is used with a rotating anode as in Fig. 58b.

Siphon.—When the deposition is complete, it is often necessary to remove the electrolyte without stopping the current, otherwise partial dissolution of the deposit would occur. This is most easily accomplished in the case of a basin electrode by means of a siphon arranged as shown in Fig. 59. The short

limb of the siphon should reach to the bottom of the basin, and to prevent abrasion it should be covered with a short piece of rubber tubing. The longer limb should be fitted with a rubber tube and spring-clip by means of which the rate of outflow

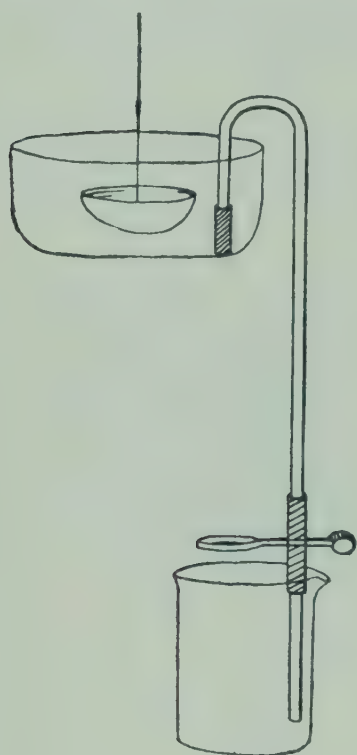


FIG. 59.

may be regulated. To start the siphon, fill it with water, place it in position, and open the clip. Run water into the basin from a tap-funnel to replace the solution withdrawn. The water must be allowed to flow gently onto the surface of the solution, so that there is as little mixing as possible. When about 200 ml. of water has been used, stop the current, disconnect the apparatus, and complete the washing in the usual manner with the wash-bottle.

Measurement of Current.—An ammeter reading up to 5 or 6 amperes (not necessarily very accurately) and a high-resistance voltmeter recording up to 10 volts are required.

Regulation of Current.—It is necessary to have some form of adjustable resistance, such as a rheostat with a sliding contact, in the circuit. A rheostat with a maximum resistance of 20 ohms will be found suitable for most purposes.

Arrangement of Apparatus.—The positive pole of the battery is connected to the anode, and the negative pole to the cathode, a rheostat and ammeter being inserted in series. If measurements of difference of potential in the electrolytic cell are required, the voltmeter is connected across the electrodes (Fig. 60).

Electrolytic Determination of Copper (With Stationary Electrodes)

Copper is readily deposited from a copper sulphate solution by electrolysis, and forms a coherent deposit if the potential used is not above 2.2 volts. Further, the copper under these conditions is deposited in a pure state, even when the solution contains iron, nickel, and other metals. The time required for complete deposition is greatly increased when iron is present in the solution, but the precipitation is almost quantitative,

even in presence of 1 gram of iron, if sufficient time is allowed. Nitrate and chloride interfere with this method, and if these ions are present the solution must be evaporated with 2 to 3 ml. of concentrated sulphuric acid until complete conversion into sulphate is effected, and dense white fumes are evolved.

Procedure.—Clean the platinum basin by thorough washing and ignition, cool, and weigh.

Weigh out accurately about 1.3 gram of copper sulphate, dissolve in water in the tared platinum basin, dilute the solution to 100 ml., and add about 5 ml. of dilute sulphuric acid. Use

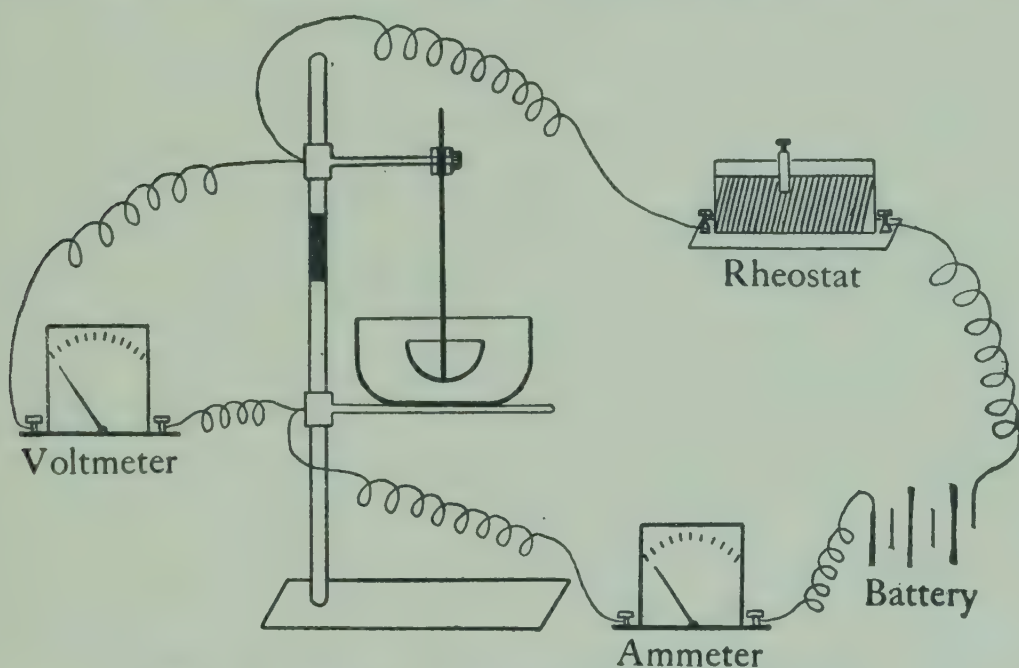


FIG. 60.—General Arrangement of the Apparatus.

as an anode a sheet of platinum or a stout platinum wire. Cover the basin with a clock-glass cut into two pieces and provided with a notch for the anode wire. Connect the electrodes with an accumulator, without any intermediate resistance, and allow the current to pass for about twelve hours. It is often convenient to start the experiment late in the day and allow the current to pass all night.

Next morning, rinse the drops on the underside of the clock-glass into the basin and allow the electrolysis to continue for another hour. Switch off the current, remove the anode and rinse it quickly, and immediately pour the solution into a beaker. Without delay, rinse the basin several times with water, and then twice with acetone (reject the acetone washings). Dry the basin in the steam-oven for not more than ten minutes, then cool, and weigh.

Remove the deposit from the basin by means of hot, dilute nitric acid, ignite and weigh the basin again. Pour back the solution and pass the current again for an hour, and reweigh. (Any further deposit of copper will be readily seen on the clean surface of the platinum.) If the weight is unchanged, it may be assumed that all the copper is deposited.

Electrolytic Determination of Copper

(With a Rotating Electrode)

The main object of employing a rotating electrode for this determination is to bring about a continuous movement of the electrolyte at its surface, thus preventing local depletion of copper ions, with the resulting evolution of hydrogen, at current densities sufficiently high for rapid electrolysis. A further advantage lies in the fact that the deposition of copper may be carried out in a solution containing nitric acid, which is used in dissolving copper alloys and ores, as with a rotating electrode any local concentration of nitrous acid formed by reduction is prevented. The previous removal of nitrate by evaporation with sulphuric acid may therefore be dispensed with.

The following method for the determination of copper is convenient and accurate, and it may be used to separate copper from cobalt, nickel, zinc, and iron. The solution must contain about 3 per cent. of nitric acid. It must be free from chloride and from more than a trace of nitrite, both of which may be removed, if necessary, by evaporation with sulphuric acid (p. 432).

The main difficulty in this method is to prevent dissolution of copper during the washing process; this is caused by *nitrous* acid, formed by electrolytic reduction of the nitric acid. If the nitrous acid is destroyed by adding a little hydrogen peroxide or urea, just before interrupting the current, no copper is redissolved by the nitric acid.

Procedure.—A suitable amount of copper for deposition is about 0.25 gram. If it is in the metallic form, it is dissolved in a 150 to 200 ml. narrow beaker, in 10 ml. of concentrated nitric acid diluted with 10 ml. of water. The solution is boiled to expel oxides of nitrogen. The free acid is neutralised with ammonia, 3 ml. of concentrated nitric acid are added, and

the solution diluted to about 100 ml. To destroy any nitrous acid that may still be present, add half a gram of urea and warm. If the copper is already in solution, any free acid is neutralised with ammonia, and 3 ml. of concentrated nitric acid are added. The solution is then diluted to about 100 ml.

The cathode is cleaned in hot dilute sodium hydroxide followed by dilute nitric acid, rinsed with water and finally with alcohol or acetone. It is dried in a steam-oven and weighed. The electrodes are fitted up, and connected in a circuit as described on p. 270, four lead accumulators being used. The motor driving the rotating chuck is started, and the electrodes adjusted if necessary. The beaker containing the copper solution is now raised until the cathode is almost completely immersed. It is covered by the two halves of a watch-glass, through the centre of which a suitable hole has been bored before the splitting of the glass. The motor is restarted and allowed to run at such a speed that the anode is rotating at about 800 revs. per min. The current is now switched on, and adjusted to about 0.5 ampere until a layer of copper has been deposited on the cathode, when the current is raised to 3 amperes. The progress of the electrolysis can be gauged from the colour of the solution. When the solution is colourless, rinse the undersides of the watch-glass into the beaker, and after a few minutes test 1 drop of the solution with ammonia and sodium diethyldithiocarbamate to find whether all the copper has been deposited. Add 1 gram of urea, and after a minute reduce the current to half an ampere. Remove the beaker and rapidly replace it with one containing distilled water. Stop the motor, cut off the current, disconnect the electrodes, and wash the cathode with acetone. Dry in a steam-oven, and weigh.

Electrolytic Determination of Nickel

If copper is present in the original solution, it must be removed by deposition from an acid solution, as already described. If nitrate is present, it must be removed by evaporation with concentrated sulphuric acid (p. 432). Chloride and sulphate do not interfere with the process.

Procedure.—The amount of substance taken should preferably be such as will yield about 0.3 gram of nickel. Make

the solution approximately neutral, add 5 grams of ammonium sulphate and 20 ml. of concentrated ammonia, and dilute to about 120 ml.

The arrangement of the apparatus should be exactly as described above for the determination of copper with a rotating cathode, except that the beaker containing the solution must be supported above a wire gauze.

By means of a small flame, raise the temperature of the solution to 60° - 80° , and keep it between these limits during the electrolysis. Use three or four accumulator cells, and adjust the initial current to about 0.5 ampere. Increase the current gradually to about 3 amperes. When the solution is colourless, rinse the watch-glass into the beaker, and after a further five minutes test for nickel in 1 drop of the solution by the addition of dimethylglyoxime.

When all the nickel is deposited, reduce the current to about 0.5 ampere and rapidly replace the beaker by one containing distilled water. Stop the motor, switch off the current, and finish the determination as in the case of copper above.

Exercise.—Determine the percentages of copper and nickel in a sample of "Constantan" wire, or "Monel" metal. Dissolve a weighed portion (about 0.5 gram) in 10 ml. of concentrated nitric acid mixed with an equal volume of water. Boil the solution for a few minutes, neutralise with ammonia, add 2 to 3 ml. of concentrated nitric acid and 0.5 gram of urea, and dilute to 100 ml. Deposit and weigh the copper as described above. The water used for washing the electrodes is added to the electrolysed solution, and the whole evaporated with sulphuric acid to remove nitrate (see p. 432). Dilute, and determine the nickel as described above, omitting the addition of ammonium sulphate.

Electrolytic Determination of Cadmium

Cadmium is readily deposited electrolytically from solutions of most cadmium salts, but in order to obtain a pure coherent deposit it is best to use a solution of potassium cadmium cyanide.

Procedure.—To the cadmium solution, containing 0.3 gram of cadmium, add 1 ml. of phenolphthalein solution, and then

pure 2N sodium hydroxide solution until a pink coloration is produced; then add a further 2 to 3 ml. While stirring the solution, add slowly a 5 per cent. solution of potassium cyanide until the precipitate produced at first is redissolved. An additional 10 ml. are then added.

Dilute to 100 ml., and electrolyse the solution, using a rotating anode, at 70°. It is advisable, though not essential, to deposit a layer of copper upon the cathode before the cadmium. The electrolysis and washing are carried out as described for copper (p. 272), except that the initial current should not exceed 0.2 ampere. The current is later raised to 3 amperes, and after three-quarters of an hour 1 ml. of the solution is tested for cadmium by boiling with dilute hydrochloric acid to remove cyanide (CARE!), diluting, and passing hydrogen sulphide through the test solution. The cathode is dried and weighed in the usual manner.

Electrolytic Determination of Zinc

The most satisfactory electrolyte for the deposition of zinc is an alkaline zincate solution, containing excess of alkali. If a nitrate is present, it must be removed by evaporation with sulphuric acid (see p. 432). Ammonium salts, if present, must be decomposed by addition of excess of potassium hydroxide and boiling.

Zinc must not be deposited directly on platinum, and if a platinum cathode is to be used, this must be first covered with a layer of copper by electrolysis of copper sulphate, and the electrode washed, dried, and weighed.

Procedure.—To a solution of zinc sulphate containing 0.3 to 0.4 gram of zinc, add sodium hydroxide solution to neutralise any free acid, and then 8 to 10 grams of solid sodium hydroxide. Dilute the solution to about 100 ml., and using a rotating anode begin the electrolysis with a current of 0.5 ampere. After five or ten minutes raise the temperature to 60°, and increase the current to 2 amperes. When the electrolysis has proceeded for three-quarters of an hour, test 1 ml. of the solution with sodium sulphide to ascertain whether the deposition is complete. As the deposited zinc is liable to oxidise rapidly in air when wet, the electrolyte is best removed by means of a siphon (see p. 270). Drying must be carried out

at as low a temperature as possible, and washing with acetone or ether after alcohol is to be recommended for this reason.

Electrolytic Determination of Lead

Lead is always deposited as lead dioxide on the anode, and to prevent any separation of metallic lead on the cathode, a high concentration of nitric acid must be used. In the presence of a considerable amount of copper, however, a lower concentration of nitric acid is permissible as the deposition potential of metallic lead is not likely to be reached. Manganese interferes with the estimation of lead by this method and certain other metals may possibly contaminate the deposit, rendering it advisable in the presence of much impurity to dissolve and redeposit the lead dioxide. Chlorides must be absent.

Procedure.—To a solution of lead nitrate, containing about 0.3 gram of lead, add 15 to 20 ml. of concentrated nitric acid, and dilute to 85 to 100 ml. Before assembling the electrodes, clean the anode, dry at about 200° in an air-oven, and weigh. Heat the electrolyte to 50°, and adjust the current to about 3 amperes. After forty-five minutes, test 1 ml. of the liquid with sodium sulphide after neutralising. When the electrolysis is finished, stop the motor, and displace the electrolyte by distilled water, using a siphon as described on p. 270. Continue washing until the liquid is almost free from acid, stop the current, and disconnect the anode. Rinse with distilled water, and dry as above. Even at 200° a trace of water is retained by the lead dioxide, making the result about 0.25 per cent. too high. If the anode is dried at 120° the empirical factor $Pb/PbO_2 = 0.864$ should be used.

To remove the lead dioxide from the anode, place this in warm moderately concentrated nitric acid, containing a little glucose or oxalic acid.

Electrolysis with Stationary Electrodes

If preferred, the electrolyses above may be carried out with stationary electrodes. Smaller current densities must be used, and the duration of the electrolysis greatly increased. For a general outline, see the determination of copper with stationary electrodes (p. 270).

Electrolytic Analysis of Brass

OUTLINE OF METHOD.—The *copper* and *lead* are deposited simultaneously on the cathode and anode respectively. The *iron* is precipitated with ammonia, and weighed as ferric oxide. The *zinc* is then deposited on the cathode from alkaline solution. The *tin* is determined in a separate portion as metastannic acid.

Procedure.—Dissolve not more than 1 gram of the alloy in a mixture of 5 ml. of concentrated nitric acid and 10 ml. of water in the beaker to be used for the electrolysis. Dilute to about 60 ml., and boil for a few minutes to remove oxides of nitrogen. If the solution is not clear, because of the presence of metastannic acid, filter into another beaker of the same size, washing the filter and neglecting the residue. Whether filtration has been necessary or not, dilute the solution to about 80 ml., and add 5 ml. of concentrated nitric acid. Electrolyse with a rotating anode, both anode and cathode being of platinum gauze and weighed before the experiment. Heat to 60°, and carry out the electrolysis as described for the deposition of lead (p. 276). After thirty minutes, by which time most of the lead present in the alloy will be deposited as lead dioxide on the anode, cool, and dilute to 160 ml. Finish the electrolysis as described for the deposition of copper (p. 272). Wash and dry the electrodes, and weigh them as directed on pp. 273 and 276. Leave the copper deposit on the cathode.

Precipitate the iron from the solution, after the deposition of the copper and lead, by double precipitation with ammonia as described on p. 415, and weigh the iron as Fe_2O_3 or determine the iron colorimetrically as on p. 290.

Evaporate the combined filtrate and washings from the iron precipitation to about 100 ml., add 4 ml. of sulphuric acid, and 25 ml. each of nitric and hydrochloric acids, and evaporate to fumes of sulphur trioxide. Cool, dilute to 100 ml., add 16 grams of sodium hydroxide, and deposit the zinc on the cathode (already covered with copper) as described on p. 275.

The tin may be determined on a separate portion of 5 grams of the alloy as described on p. 419.

PART IV

PHOTOMETRIC METHODS

THE determination of a very small quantity of a substance is frequently necessary, and it is often found that one of the photometric methods is by far the easiest and most accurate. The relative error of these methods is generally greater than that associated with the determination of large quantities by ordinary means and will usually be of the order of 1 to 2 per cent. or even more. Sometimes, however, the principle of differential spectrophotometry may be applied, and the precision attainable will then compare favourably with that of normal macro-methods.

Photometric methods are based on the absorption or the scattering of light by solutions or suspensions. The determination of the amount of white light absorbed by a solution is called *colorimetry*. If light of a definite wavelength is used, the process is called *spectrophotometry*. Sometimes light of a definite colour, covering a narrow band of wavelengths, is used. Analysis based on the measurement of light scattered by a suspension is called *nephelometry*. When a solution or solid is irradiated with ultra-violet light and the radiation emitted at a different wavelength is measured, the process is called *fluorimetry*.

It is found that those substances which absorb electromagnetic radiation do so in different proportions at different wavelengths. If the percentage of light absorbed by a substance or the optical density is plotted against the wavelength of the incident radiation, the resulting curve is referred to as an *absorption spectrum*. A typical example, the absorption spectrum of a solution of murexide, is shown in Fig. 61.

Theory of Colorimetry.—When monochromatic or heterogeneous light falls on a homogeneous substance, part of the incident light is reflected, part absorbed, and the rest transmitted. If the intensity of the incident light is denoted by I_0 ,

that of the reflected light by I_r , that of the absorbed light by I_a , and that of the transmitted light by I_t , then :

$$I_o = I_r + I_a + I_t.$$

I_r is usually eliminated by comparing the intensities of light beams transmitted through the solution and the solvent contained in similar cells. It is customary to measure the intensity of the light beam after it has passed through the solvent and to regard *this* intensity as being the same as the intensity of the incident beam. This must be borne in mind during the

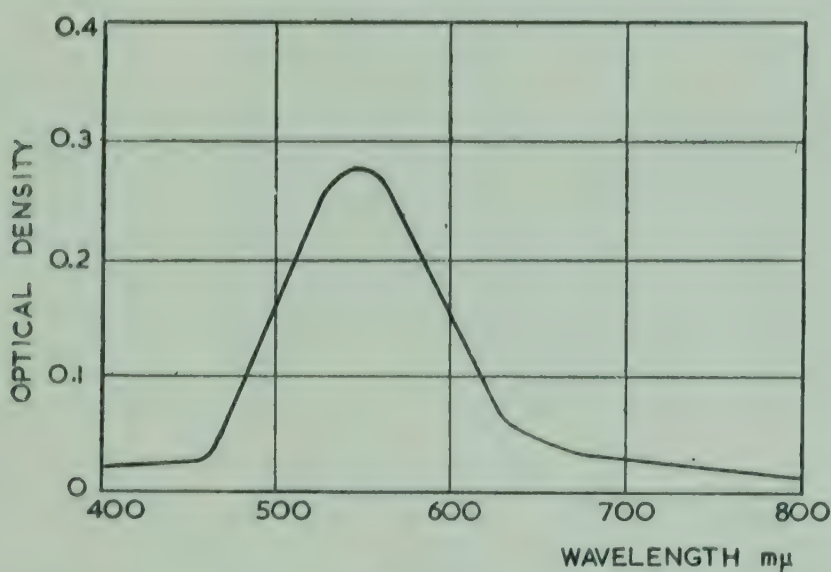


FIG. 61.

subsequent development of the theory. In the case where I_r is eliminated the relation becomes :

$$I_o = I_a + I_t.$$

Colorimetry and spectrophotometry are based on the laws of Lambert and of Beer.

Lambert's Law.—When monochromatic radiation passes through a thin layer of a transparent medium, the fraction of it absorbed by the layer is proportional to the intensity of the incident radiation and to the thickness of the layer. This may be expressed as a differential equation :

$$-\frac{dI}{dt} = kI$$

where I is the intensity of the incident radiation, t is the thickness

of the medium, and k is a proportionality constant. Integrating this equation we get :

$$I_t = I_o e^{-kt}.$$

Transforming to Briggsian logarithms we have :

$$I_t = I_o 10^{-k't}.$$

where k' has the value of $0.4343k$; k' is usually called the *extinction coefficient* (Bunsen and Roscoe, 1857) and is the reciprocal of the thickness of medium, in centimetres, required to reduce the intensity of the transmitted light to one-tenth of that of the incident light.

Beer's Law.—So far we have discussed light transmission as a function of the thickness of the absorbing layer only. Beer's contribution was to study the effect of the concentration of a coloured compound in solution on the light transmission. He found the same relation between transmission and concentration as Lambert found between transmission and thickness of the layer. We can write this as a differential equation :

$$-\frac{dI}{dc} = KI$$

where c is the concentration and K is a constant.

On integration and transformation as before we get :

$$I_t = I_o 10^{-K'c}.$$

We can combine the equations derived from these two laws, and write (the Beer-Lambert Law) :

$$I_t = I_o 10^{-\epsilon ct} \quad \text{or} \quad \log I_o/I_t = \epsilon ct$$

where ϵ is a constant of which the value depends on the units used to express the concentration. If c is expressed in molarity, ϵ is called the *molar extinction coefficient*, and is the reciprocal of the thickness in centimetres of a 1 molar solution at which the intensity of the transmitted light is one-tenth that of the incident light. The ratio I_t/I_o is called the *transmission*, and it is the fraction of the incident light that is transmitted by the medium. The reciprocal of the transmission is the *opacity*, and the logarithm of the opacity is termed the *optical density*. Synonyms for optical density are *absorbance*, *absorbancy*, *extinction*.

Consider now two solutions of a coloured substance and suppose that their concentrations are c_1 and c_2 . Let them be placed in a colorimeter (see p. 284) which permits the depth of the layers to be changed and measured easily, and allows the amounts of light transmitted to be compared. When the two layers have the same intensity of colour then :

$$I_{t_1} = I_{t_2} = I_0 10^{-\epsilon c_1 t_1} = I_0 10^{-\epsilon c_2 t_2}$$

where t_1 and t_2 denote the depths of the columns of the solutions with concentrations c_1 and c_2 .

Under these conditions, if Beer's law holds, then :

$$c_1 t_1 = c_2 t_2.$$

The colorimeter may, then, be used to investigate Beer's law by changing c_1 and c_2 and observing whether the last expression holds, or it may be used to determine the concentration of a coloured solution by comparison with a solution of known concentration. It must be remembered that the last equation holds only if Beer's law is obeyed and the instrument used has no optical defects.

If a spectrophotometer is used, the length of the light path through the medium can be kept constant and the optical density can be determined directly. In this case, if Beer's law holds, a plot of concentration against optical density will produce a straight line which passes through the origin.

Deviations from Beer's Law.—The factors that may cause deviation from Beer's law include :—

(1) Large amounts of electrolytes may change the value of the extinction coefficient or may cause a shift of the wavelength at which maximum absorption occurs ; both effects may occur simultaneously.

(2) Electrolytes may be present that react chemically with the coloured components of the solution.

(3) Dissociation or association phenomena may occur, in which case the nature of the species present in solution will vary with the concentration. In this connection the possible effects of change in hydrogen ion concentration must be considered, especially when dealing with the coloured anions of weak acids or the coloured cations of weak bases.

(4) Complexes may be formed which have colours different from those of the original compounds. This behaviour can

sometimes be turned to advantage; it is often possible to eliminate the interference of coloured ions by converting them into colourless complexes.

In general, the most satisfactory reactions for use in colorimetric methods are those which produce colours that are stable for a considerable period of time, and are not greatly affected by changes in the concentration of reagent or other salts present, by small changes in pH , or by changes in temperature of several degrees.

In colorimetric work it is usually desirable (1) that the solutions to be compared contain as far as possible the same quantities of admixed substances, (2) that they are at the same temperature, (3) that they are diluted to the same volume before adding the reagent, and (4) that the order in which the reacting substances are mixed, and the time allowed before the comparison is made, are as nearly the same as possible. It is necessary that the solutions should be free from any suspension or turbidity. No other coloured substances should be present.

Methods of Determination

Visual Methods.—Several methods are available for visual determination of the depth of colour of a solution.

(1) The standard series method. The sample solution is diluted to a definite volume and its colour is compared with the colours of a series of standards prepared in a similar way and diluted to the same volume. Usually the colour of the sample will be found to lie between those of two of the standards; a fresh series of standards can then be prepared, covering the interval between these two. By successive approximations of this type the depth of colour may be estimated to the desired degree of accuracy.

(2) For this method cylinders of colourless glass (Nessler tubes) may be used. These tubes are usually graduated to contain 50 ml. or 100 ml., and the graduation mark must be at the same level in all tubes of equal capacity. In order to exclude side light, it is worth while providing the tubes with opaque covers open at the ends and made from stout brown paper. A glass tube on which a flattened bulb of appropriate size is blown (Fig. 62) should be used for mixing the solutions in the tubes. The colour intensities are compared by holding

the tubes close together over a white surface (*e.g.*, a sheet of opal glass) and looking down into the tubes. A stand similar to a test-tube rack, having an opal glass base and holes for six Nessler tubes, is obtainable for the purpose.

There is for each substance a depth of colour which is most suitable for matching. A solution is prepared in a Nessler tube containing the correct amount of standard substances to give this depth, adding the reagents in the prescribed order. A preliminary determination of the strength of the unknown solution is made by adding it from a burette to another Nessler tube containing the reagents diluted with a convenient amount of water until approximately the same depth is obtained. The volume of solution added is observed and the liquid rejected. Into the Nessler tube this volume of the solution is now run, and the reagents added in the same order as in the case of the standard. The depth of colour obtained will probably be found to be slightly different from that of the standard. Other standards are prepared, containing slightly more or less of the standard solution, the reagents being added in the same order, until an exact match is obtained.

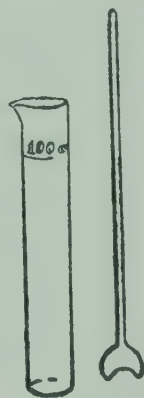


FIG. 62.

To most observers the solution in the tube held in the left hand appears slightly darker in colour than that in the right, even when the two tubes are filled with portions of the *same* solution. It is a good plan therefore, in colorimetric comparisons generally, to interchange the tubes, and if the left-hand tube always appears the darker, it may be assumed that the intensities of the colorations are equal.

(3) A fixed amount of the reagent is diluted with a suitable volume of water, and a measured volume of the unknown solution added. An equal amount of reagent in another tube is diluted almost to the same volume, and a standard solution of the substance to be estimated is added until, after mixing, the depth of colour matches that of the unknown.

(4) To a measured quantity of the sample a definite amount of reagent is added, and it is then diluted to some known volume, and placed in a cell with parallel sides. A solution for comparison, having the same total volume, is prepared, using an equal amount of reagent and a measured volume of a standard solution of the substance to be estimated. This solution should be slightly deeper in tint than the one which is being

determined. The sample solution is poured into a similar rectangular cell of the same dimensions. Water is added from a burette to the deeper-coloured solution until the colours in the two cells appear to be of equal depth when the cells are viewed from the side. The initial concentrations are directly proportional to the final volumes, provided that the dilution of the darker liquid has not caused any change in the amount of coloured substance present.

(5) In this method a match is obtained by altering the observed length of one of the columns of liquid until it matches a fixed length of the other. For the method

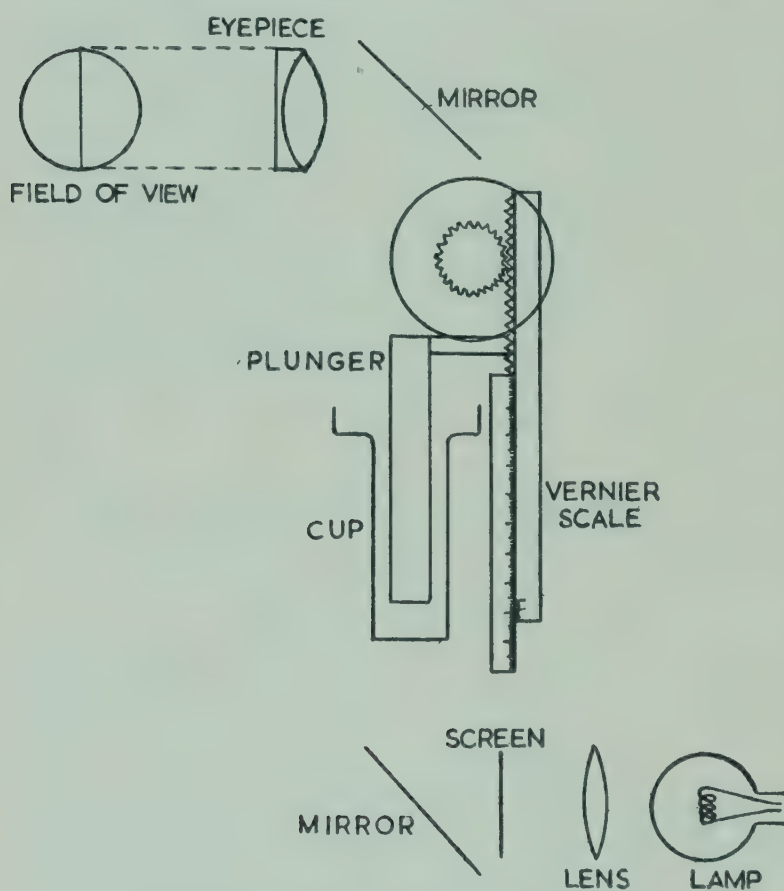


FIG. 63.—The Schreiner Colorimeter.

to be accurate the depth of colour of the two liquids should be nearly equal. The two liquids are placed in similar tubes, and the length of the column of the darker solution is reduced until the colours of both appear to be equal when viewed down the tube. The ratio of the lengths of the columns after matching will be equal to the inverse ratio of the concentrations. This

method is most suitable for use with a colorimeter.

Generally in colorimeters a plunger tube is used to shorten the observed column of liquid in one of the comparison vessels, but in some the length of column is reduced by withdrawing liquid from one of the comparison tubes. In the instrument illustrated (Fig. 63) the comparison tubes are fixed, and the plungers may be raised or lowered until the depths of colour appear to be matched. The cups have black glass walls (to exclude extraneous light) and clear glass bases. The plungers are operated by a rack and pinion,

and the depth of liquid between the end of the plunger and the base of the cup can be read on a vernier scale. The use of two plungers made of similar material compensates for any colour effects associated with the glass of the plungers. Light from a common source is passed upwards through the two liquids and the plungers and is then reflected into an eye-piece so that the two halves of the field of view represent the colours of the two solutions.

A number of precautions must be observed in the use of the colorimeter. There are usually small differences in the optical characteristics of the cups and plungers, and the procedure must be designed to eliminate this source of error. First the evenness of illumination must be checked. Both cups are filled with distilled water, and placed in the instrument. The plungers are set at the same depth in the water, and the position of the illuminating lamp is adjusted until the two halves of the field appear to be evenly lighted. The cups are removed and the plungers are wiped dry with absorbent tissue; the distilled water is then replaced in both cups by the standard solution. The plunger in one of the cups, say the left-hand one, is set at a definite depth, and is *left there for the remainder of the procedure*. In the other cup the plunger is first lowered to the bottom of the cup and the scale is read to find whether zero depth of liquid is in fact recorded. The plunger in this cup is then raised until the intensities of colour in the two halves of the field appear to be matched. The scale reading is taken and the matching repeated about ten times in such a way that the balance is approached from either side an equal number of times. This procedure is adopted to reduce eye fatigue and to eliminate as far as possible any bias resulting from fatigue. The average of the readings is taken. The cup is then removed, rinsed and filled with the sample solution, and replaced after the plunger has been wiped dry. The balancing is then repeated in the same way, and the average depth for the sample is calculated. In this way the sample and standard solutions are compared with the same solution, and any bias arising from optical defects is eliminated.

Photoelectric Methods.—In these methods the human eye is replaced by a photoelectric cell, and the optical density of the solution is measured directly, instead of the intensity of colour being compared with that transmitted by a standard

solution. The concentration of the solution can then be read from a calibration curve relating optical density to concentration. The principle of the method remains the same although there exists a variety of instruments for applying it. These instruments may be divided into two groups, filter photometers, and spectrophotometers. In filter photometers incident radiation covering a small range of wavelengths is obtained by passing white light through a suitably coloured filter. Sometimes the same effect is achieved by the use of a diffraction grating, in which case the instrument is known as an abridged spectrophotometer. In either case the incident beam passes through a cell containing the solution and then falls on a photoelectric cell. The current generated by the cell is proportional to the intensity of the light incident on it, and it can be measured in a potentiometric circuit. The intensity of the light transmitted by the solution is compared with that transmitted by the solvent contained in a similar absorption cell. Obviously, any fluctuations in the intensity of the light source will produce small errors in the results. In some instruments this source of error is eliminated by using two photoelectric cells simultaneously, matched for spectral response and sensitivity; the solution is placed in front of one cell and the solvent in front of the other, and their outputs are balanced in a bridge circuit. The difficulty here is to obtain the matched photoelectric cells.

In spectrophotometers the incident radiation is almost monochromatic, the band width usually being of the order of a few millimicrons ($1 \text{ m}\mu = 10 \text{ \AA}$). This narrow band of wavelengths is obtained by means of a light source and a prism. The principle of operation is the same as that for a filter photometer, but the amount of incident radiation is usually so small that an amplifying stage is needed between the photoelectric cell and the measuring circuit.

The great advantage of the photoelectric instruments is that they may be used to make measurements not only in the visible part of the spectrum but also in the ultra-violet and the near infra-red, so that spectrophotometric methods of analysis may be used for "colourless" solutions, provided that they absorb radiation of a wavelength within the range of the instrument.

There are a few important points to be noted in the procedure used with these instruments. The wavelength at which measure-

ments are to be made should be chosen in a region where there is no sharp change of the extinction with change of wavelength. If there is a sharp change, a small error in setting the wavelength will cause a large error in the apparent optical density. The wavelength chosen should preferably be one at which the extinction coefficient is at a maximum. The choice of concentration is important because it affects the accuracy attainable. It can be shown (see, for example, Kolthoff and Sandell, *Quantitative Inorganic Analysis*, 3rd Edition, p. 631) that the relative error arising from instrumental measurements in a spectrophotometric determination is fairly constant for 13 to 70 per cent. transmission, but it increases rapidly outside these limits. In order to keep observational errors at a minimum therefore, it is necessary to arrange that the optical density should be between 0.15 and 0.90.

Differential Spectrophotometry.—Sometimes it is possible to reduce the observational error to quite small proportions by using a solution of high optical density and comparing its transmission, not with that of the solvent, but with that of a solution of accurately known concentration and similar optical density. The observed relative transmission is then proportional to the difference in concentration between the solution and the reference standard. In theory an unlimited increase in precision is attainable by using solutions of sufficiently low transmission, but in practice the gain is limited. Full-scale readings for solutions of low transmission can be obtained only with wide band-widths; the use of these leads to deviations from Beer's law which decrease the sensitivity. Secondly, stray radiation from scattering and reflection seriously affects measurements of very small transmissions. The method is, however, capable of yielding a precision of 1 to 3 parts per 1000 in favourable circumstances.

Nephelometry.—When light passes through a turbid medium it undergoes a reduction in intensity caused partly by absorption by the particles in the suspension and partly by reflection and refraction. The concentration of a suspension can be measured either by measurement of the amount of light transmitted (*turbidimetry*) or by measurement of the amount of light scattered (*nephelometry*). For turbidimetric measurements a suitable colorimeter or spectrophotometer may be used, but it must be remembered that Beer's law holds only for very thin layers of a suspension or for very dilute suspensions. In nephelometers measurement is made of the amount of light scattered

at right angles to the incident beam, and the sample is compared with a standard of known concentration.

Nephelometric methods are generally less accurate than colorimetric ones, because of the difficulty of forming suspensions of reproducible characteristics. The important factors involved in achieving this include (1) the concentration of the two ions which combine to produce the precipitate, (2) the ratio of concentrations in the solutions mixed, (3) the rate and manner of mixing, (4) the time required to produce maximum scattering, (5) the stability of dispersion, (6) the temperature, and (7) the effect of other substances present.

Fluorimetry.—Some compounds have the property of absorbing radiation and emitting a radiation of different wavelength; the phenomenon is known as fluorescence. Comparatively few inorganic compounds are fluorescent in solution, but fluorescence is exhibited by many compounds formed by inorganic cations and organic reagents. It is possible to detect very small amounts of material (concentrations as low as 10^{-10} g./l.) by this method. At low concentrations the intensity of fluorescence is proportional to the concentration, but as the concentration increases the intensity usually reaches a maximum and then decreases. As a rule this is a result of self-quenching, partly because the energy absorbed by the fluorescing substance from the exciting radiation is not entirely converted into emitted radiation, the remainder being absorbed by the vibrational and rotational degrees of freedom of the compound and partly from collision quenching by the substance itself. Quenching may also arise from the presence of other substances with marked specific quenching effects, but in this case the quenching is caused by conversion of excitation energy into heat energy by absorption of energy occurring during collisions of the two species concerned. Foreign substances may also reduce the intensity of fluorescence by absorbing the exciting radiation or by absorbing the emitted radiation. Some substances may increase the amount of fluorescence; this is referred to as enhancement.

For quantitative work it is usual to use ultra-violet light as the exciting radiation, and measurement is made of the intensity of radiation emitted at right angles to the incident beam. The factors that are important in fluorimetric analysis include (1) the concentration of substance, (2) the wavelength of the incident

radiation, (3) pH , (4) the temperature, (5) the presence of other fluorescent substances, (6) the presence of quenching agents or enhancing substances.

Range of Application of Photometric Methods.—Provided that a high degree of precision is not required, photometric methods can be applied to determine substances present in amounts ranging from about 10^{-5} per cent. upwards. In exceptional cases as little as 10^{-10} per cent. may be determined. The precision to be expected is generally of the order of 20 parts per 1000, although this may be improved to 1 to 3 parts per 1000 if differential spectrophotometric methods can be applied. In the case of the determination of very small amounts the error will be considerably greater ; it is difficult to estimate an upper limit for it.

Interfering substances.—In photometric work it is obviously desirable that the methods used should be as selective and free from interferences as possible. This cannot always be achieved in practice, but it is often possible to make allowance for interfering substances. If the interference cannot be eliminated by a separation or by forming a complex of the interfering substance, it may be possible to measure the total absorbance, destroy the colour of the substance to be determined, and measure the absorbance of the interfering substance alone. The absorbance of the substance sought is then obtained by simple subtraction. Failing this method, it may be found that the interfering substance has an absorption peak at a wavelength at which the substance sought has not. A correction may then be made by measuring the absorption of the sample and a standard solution of the interfering substance at the two wavelengths, and calculating the correction by simple proportion.

METHODS OF ANALYSIS

In the first three examples given below an outline is given of the procedure for visual colorimetry, filter photometry, and spectrophotometry. All three methods may be applied in the colorimetric methods described, the choice depending on the equipment available to the analyst. No attempt has been made to give an exhaustive list of the different methods available for each element ; usually one method has been selected for each.

Iron

Three methods will be described for the determination of iron. In the first, the thiocyanate method, ferric iron is determined. In the other two, the thioglycollate and *o*-phenanthroline methods, ferrous iron is the reactant.

The thiocyanate method may be used to determine ferric iron in the presence of ferrous, and the *o*-phenanthroline method to determine ferrous iron in the presence of ferric.

Thiocyanate Method

Ferric iron reacts with thiocyanate ions to form a red colour. The reaction is a complex one ; a series of complexes of the type $[\text{Fe}(\text{CNS})_x]^{+3-x}$, where $x = 1 \dots 6$, can be formed. The reaction is not ideal for colorimetric work because the colour intensity depends on such factors as the excess of thiocyanate, the amount and kind of acid present, the time of standing, etc., and the system does not in general follow Beer's law. It is necessary to use a standard having about the same iron concentration as the sample or to use a calibration curve.

The method is liable to interference from the following groups of ions :—

- (1) Fluoride, oxalate, metaphosphate, pyrophosphate, etc., which form complexes with ferric iron in acid solution. Sulphates and phosphates interfere only if present in considerable amounts.
- (2) Silver and mercurous mercury which produce insoluble thiocyanates.
- (3) Mercuric mercury, cadmium, zinc, and tervalent antimony, which form complexes with thiocyanate, and so reduce the intensity of the iron-thiocyanate colour.
- (4) Bismuth, copper, ruthenium, osmium, and molybdate, which yield colours with thiocyanate.
- (5) Nickel, cobalt, platinum, titanium, stannous tin, and arsenates may also interfere.

When large amounts of interfering elements are present, the iron may be initially separated, or the iron-thiocyanate complex may be extracted by an organic solvent and this solution used for the determination.

The following solutions are required :—

(1) *Standard Iron Solution*.—Dissolve 0.862 g. of ferric ammonium sulphate in water, add 10 ml. of concentrated hydrochloric acid, and dilute to 1 litre. One ml. of this solution is equivalent to 0.100 mg. of iron.

(2) *Ammonium Thiocyanate Solution*.—Dissolve 50 g. of the pure salt in 100 ml. of water.

Procedure.—The iron to be determined must be present in the ferric state. Oxidation is achieved, if necessary, during the preparation of the sample solution, by means of dilute potassium permanganate solution or bromine water. The best depth of colour for matching is obtained with about 0.1 mg. of iron in the volume of solution contained in the Nessler tube.

Oxidise the sample solution and dilute it to 100 ml. in a volumetric flask. Fill a 50 ml. burette with this solution. Pipette accurately 1 ml. of standard solution into a Nessler tube, add 10 ml. of dilute hydrochloric acid (2N free from iron), dilute to the 100 ml. mark, add 5 ml. of the ammonium thiocyanate solution, and mix. To a second tube add 10 ml. of dilute hydrochloric acid, about 50 ml. of water, and 5 ml. of ammonium thiocyanate solution, and mix. Add sample solution from the burette until the depth of colour after mixing is about that of the standard, but do not use more than 25 ml. of solution. Note the volume required ; if 25 ml. was insufficient, estimate the volume that would have been required. Discard both solutions and proceed as follows :—

(1) If less than 5 ml. were required, accurately dilute a portion of the solution ten-fold and continue as directed below, in (4).

(2) If between 5 and 25 ml. were required, proceed as in (4).

(3) If more than 25 ml. were required, dilute a portion of the standard solution five-fold and proceed as in (4) but using *this* solution as the standard.

(4) Prepare the standard solution as before, subject to the proviso in (3) above. To the second tube add 10 ml. of acid and 5 ml. of thiocyanate solution as before and then add $(90-x)$ ml. of water, where x ml. is the volume of sample solution that will be required to match the standard. Add sample solution (the original or the diluted solution according to circumstances) until almost the required volume has been

added. Mix and compare with the standard and add more sample solution if necessary, in small portions, until an exact match is obtained. The amount of iron in the sample is then calculated by simple proportion.

If a colorimeter is used prepare an approximately matched pair of solutions (standard and sample) as above, steps (1) to (4), and compare by the method described on p. 285. If a photo-electric instrument is used, a filter with maximum transmission at or near $480\text{ m}\mu$ is required for a filter type instrument, or a wavelength of $480\text{ m}\mu$ is used in a spectrophotometer. Measurements must be made as soon as possible after preparation of the coloured solutions.

If an organic solvent is used to extract the iron the wavelength used may have to be slightly altered. For a 2/1 v/v mixture of amyl alcohol and ethyl ether a wavelength of $500\text{ m}\mu$ is recommended.

Thioglycollic Acid Method

When a mixture of this reagent with a solution of a ferrous salt is made alkaline with ammonia, an intense red coloration is developed. Ferric salts as such do not give this colour, but they are reduced to ferrous iron by excess of the reagent, so that the total iron present is determined. Strong bases discharge the colour; oxidising agents must of course be absent. Interferences may arise from:—

(1) Bismuth, cobalt, lead, nickel, mercurous mercury, silver, gold, and uranyl ions, which give colours with the reagent.

(2) Arsenious arsenic, cadmium, copper, stannous tin, and zinc, which bleach the iron colour.

(3) Molybdate, tungstate, nitrous acid, and cyanide.

(4) Aluminium and chromium, which precipitate as hydroxides.

Beer's law is obeyed, and the intensity of colour is independent of the concentration of the reagent and of $p\text{H}$ in the range 6 to 11. The colour is fairly stable.

Procedure.—Prepare a slightly acid solution of the sample and dilute it to 100 ml. in a volumetric flask. To another 100 ml. flask transfer an aliquot containing between 0.01 and 0.02 mg. of iron. Prepare a series of standards, in 100 ml. volumetric flasks, containing 0, 0.020, 0.040, 0.080, 0.120,

0.160, and 0.200 mg. of iron, using a ten-fold dilution of the standard iron solution already described (p. 291). Neutralise a 10 per cent. v/v solution of thioglycollic acid with ammonia solution, and add 2 ml. of it to each flask. Then add 10 ml. of approximately 3M ammonia solution to each flask, dilute each solution to 100 ml., and mix thoroughly. Determine the optical density of the solutions shortly after the colour has developed, using the standard with zero iron concentration as comparison liquid in a filter photometer, and a filter with maximum transmission at 530 to 540 m μ . Prepare a calibration curve by plotting optical density against concentration, read from the graph the concentration of iron in the sample solution, and calculate the percentage of iron in the sample. Alternatively, since Beer's law is obeyed, it is enough to measure the optical density of a standard solution containing 0.100 mg. of iron per 100 ml., and to calculate the concentration of iron in the unknown by simple proportion. The calibration curve is most useful in routine work if the method used gives reproducible results. If the method gives non-reproducible results (*i.e.* the method is sensitive to small changes in conditions) it is best to run one standard solution each time. For visual colorimetry proceed in a manner analagous to that outlined for the thiocyanate method.

o-Phenanthroline Method

A very stable red complex is formed between ferrous iron and *o*-phenanthroline. The formula of the complex is $(C_{12}H_8N_2)_3Fe^{++}$. The intensity of colour is independent of the acidity in the pH range 2 to 9; Beer's law is followed. Interference may arise from the following groups of ions :—

- (1) Silver and bismuth, which give precipitates.
- (2) Cadmium, mercury, and zinc, which form slightly soluble complexes and reduce the intensity of the iron colour.
- (3) Beryllium, cobalt, copper, molybdenum, nickel, and tin.
- (4) Tungstate and phosphate.

The following solutions are required :—

(1) *Hydroquinone Solution*.—One per cent. solution in an acetic acid buffer of about pH 4.5 (65 ml. of 0.1M acetic acid and 35 ml. of 0.1M sodium acetate) prepared as required or kept in a refrigerator and discarded when a coloration appears.

(2) *Sodium Acetate Solutions*.—1M and 0.1M.

(3) *o*-Phenanthroline Solution.—A 0.5 per cent. solution of the monohydrate in water. Warming assists dissolution.

Procedure.—Take an aliquot of the sample, containing up to 0.2 mg. of iron, and transfer it to a 25 ml. volumetric flask. To a similar aliquot add a few drops of bromophenol blue and find the volume of sodium acetate solution required to adjust the *p*H to 3.5. Add the same volume of acetate solution to the original aliquot, and then 1 ml. each of the hydroquinone and *o*-phenanthroline solutions and mix. Allow to stand for one hour to ensure complete reduction of the iron, make up to volume with water, mix thoroughly, and measure the optical density at 510 m μ . Prepare a set of standards for the range 0.0 to 0.200 mg. of iron and apply the same procedure. The standards should preferably have the same final *p*H as the sample. Find the concentration of iron in the sample by means of the calibration curve.

If a filter photometer is used the filter should have maximum transmission at 480 to 520 m μ .

Aluminium

Aluminium and ferric iron form complexes with the reagent ferron, 8-hydroxy-7-iodo-5-quinolinesulphonic acid. The aluminium complex has an absorption maximum at 370 m μ , and at this wavelength Beer's law is obeyed for small concentrations of aluminium at constant *p*H. The iron complex also absorbs at this wavelength, but the amount of absorption can be accurately determined from the absorption at 600 m μ . Interference may arise from the presence of chromium, copper, manganese, molybdenum, nickel, thorium, titanium, zinc, and zirconium.

The following solutions are required :—

(1) *Standard Aluminium Solution.*—Dissolve 1.759 g. of potassium aluminium sulphate in 100 ml. of 0.1N hydrochloric acid, and dilute to 1 litre. Dilute an aliquot ten-fold to obtain a solution containing 10.0 μ g. of aluminium per ml. Use redistilled water.

(2) *Standard Iron Solution.*—Prepare a solution as on p. 291, and dilute an aliquot ten-fold to obtain a solution containing 10.0 μ g. of iron per ml. Use redistilled water.

(3) *Ferron Solution.*—Dissolve 1.000 g. of reagent in 500 ml. of redistilled water.

(4) *Ammonium Acetate Solution*.—Dissolve 50 g. in 400 ml. of redistilled water and dilute to 500 ml.

(5) *Hydrochloric Acid*.—1N.

(6) *Nitric Acid*.—1N.

Procedure.—Transfer to a 100 ml. volumetric flask 25 ml. of a nearly neutral sample solution containing aluminium or iron, or both, up to 150 μ g. Add in the following order, mixing between additions, 4 ml. of hydrochloric acid, 4 ml. of nitric acid, 20 ml. of ammonium acetate solution, and 8 ml. of ferron solution. Dilute to 100 ml. and read the official density in 1-cm. cells at 370 $m\mu$ and 600 $m\mu$, using as comparison solution a blank containing all the reagents. Apply the procedure to 10 ml. portions of the standard aluminium and iron solutions. Calculate as follows :—

Sample iron optical density at 370 $m\mu$ =

$$\frac{\text{Sample optical density at 600 } m\mu \times \text{Standard iron optical density at 370 } m\mu}{\text{Standard iron optical density at 600 } m\mu}$$

Sample aluminium optical density at 370 $m\mu$ =

$$\text{Sample optical density at 370 } m\mu - \text{Sample iron optical density at 370 } m\mu$$

The concentration of aluminium in the sample is then calculated by simple proportion from the optical density for sample and standard.

Antimony

When tervalent antimony in sulphuric acid solution is treated with an excess of potassium iodide solution yellow iodoantimonous acid (HSbI_4) is formed. The complex has absorption peaks at 330 $m\mu$ and 425 $m\mu$. The sensitivity is greater at the shorter wavelength. Mercuric, plumbous, and bismuthyl ions are the main interfering substances at the shorter wavelength, and bismuthyl at the longer. Interference may also occur from arsenic, copper, mercury, molybdenum, nickel, tin, and tungsten.

The following solutions are required :—

(1) *Standard Antimony Solution*.—Dissolve 0.2743 g. of potassium antimonyl tartrate hemihydrate in redistilled water, add 160 ml. of concentrated sulphuric acid, and dilute to 1 litre. One ml. of this solution contains 0.100 mg. of antimony.

(2) *Sulphuric Acid Solution*.—Add 250 ml. of concentrated sulphuric acid *cautiously* to 700 ml. of water, cool, and dilute to 1 litre.

(3) *Potassium Iodide Solution*.—Dissolve 140 g. of potassium iodide and 10 g. of crystalline ascorbic acid in redistilled water and dilute to 1 litre. The ascorbic acid is added to reduce any iodine that may be liberated.

Procedure.—Prepare the sample solution so that it is slightly acid with sulphuric acid and contains from 0.15 to 1.8 mg. of antimony per 100 ml. Transfer a 10 ml. aliquot to a 50 ml. volumetric flask. Add 25 ml. of the potassium iodide reagent, and dilute to volume with the sulphuric acid solution. Mix thoroughly, and measure the optical density at 330 m μ , using silica cells, or 425 m μ using glass cells. Use a reagent blank solution as comparison liquid. Prepare a calibration curve using the standard antimony solution.

Bismuth

Bismuth can be determined colorimetrically by means of the yellow colour produced on adding a solution of potassium iodide to an acid solution containing small amounts of the metal. Beer's law is obeyed. Interference is caused by platinum, palladium, antimony, and tin, which give coloured compounds with iodide. Lead, thallium, silver, and copper, which have insoluble iodides, should be absent. Oxidising agents should be absent. Large amounts of cadmium, chloride, or fluoride, reduce the intensity of colour.

The following solutions are required :—

(1) *Standard Bismuth Solution*.—Dissolve 0.125 g. of pure bismuthyl chloride in about 20 ml. of dilute hydrochloric acid in a 100 ml. volumetric flask, dilute to volume, and mix thoroughly. Dilute 10 ml. of this solution to 1 litre, adding about 25 ml. of dilute hydrochloric acid before the dilution. One ml. of this solution contains 10.0 μ g. of bismuth.

(2) *Potassium Iodide Solution*.—Dissolve 10 g. of potassium iodide in 100 ml. of water. This solution must be freshly prepared.

(3) *Sulphurous Acid Solution*.—Dilute a saturated aqueous solution of sulphur dioxide with an equal volume of water. This solution must be freshly prepared.

Procedure.—Transfer to a 25 ml. volumetric flask a 10 ml. aliquot of the sample solution, which should be 1 to 2N in sulphuric acid and contain from 0.5 to 10 μ g of bismuth per ml.

Add 0.1 ml. of sulphurous acid and 3 ml. of potassium iodide solution, dilute to volume, and mix thoroughly. Measure the optical density at 460 m μ , using a reagent blank as comparison liquid. Prepare a calibration curve.

Chromium

Sexivalent chromium reacts in acid solution with diphenylcarbazide to give a soluble red-violet compound of unknown composition. The reaction is very sensitive and subject to little interference. Molybdenum is the only element giving a similar colour in mineral acid solution. Mercury gives a blue colour, but the reaction is only sensitive at low acidity. Iron and vanadium give yellowish colours with the reagent. Iron is often eliminated in the course of oxidising the chromium; the colour given by vanadium fades fairly rapidly, but if the vanadium-chromium ratio is greater than 10 to 1 it is better to separate the vanadium by extracting its oxinate with chloroform at pH 4.

The following solutions will be required:—

(1) *Standard Chromium Solution*.—Dissolve 0.2827 g. of potassium dichromate in water and dilute to 1 litre. Dilute 50 ml. of this solution to 1 litre. One ml. of this solution contains 0.50 μ g. of chromium.

(2) *Diphenylcarbazide Solution*.—Dissolve 0.25 g. of diphenylcarbazide in 100 ml. of alcohol. The solution is best freshly prepared.

(3) *Sulphuric Acid*.—6N, free from reducing agents. Treat the hot acid with dilute potassium permanganate until a very faint pink colour appears.

Procedure.—The sample solution may contain 0.02 to 0.5 μ g. of chromium per ml.; the chromium must be in the sexivalent state. Transfer 10 ml. of the sample solution to a 25 ml. volumetric flask, add enough sulphuric acid to make the acid concentration about 0.2N on dilution to 25 ml., mix, add 1 ml. of the diphenylcarbazide solution, and dilute to volume. Mix well, allow to stand for 10 to 15 minutes if vanadium is present, and then determine the optical density at 540 m μ , using a reagent blank as comparison liquid. Construct a calibration curve or compare direct with a single standard.

Cobalt

Nitroso-R salt (1-nitroso-2-hydroxy-naphthalene-3 : 6-disulphonic acid, sodium salt) reacts with cobalt to form a red compound which is stable in acid solution. Iron and copper interfere, and cyanide, peroxide, persulphate, and reducing agents must be absent. The interference of iron can be eliminated by oxidation and addition of sodium fluoride to form a complex with the ferric iron. Copper must be separated by precipitation with hydrogen sulphide or by extraction with dithizone.

The following solutions will be required :—

(1) *Standard Cobalt Solution*.—Dissolve 0.1000 g. of cobalt in nitric acid, and dilute to 1 litre. Dilute a portion of this solution ten-fold to obtain a solution containing 10.0 μg . of cobalt per ml.

(2) *Nitroso-R Salt Solution*.—Prepare a 0.1 per cent. aqueous solution.

Procedure.—From the sample solution, which should be free from iron and copper, transfer to a 50 ml. beaker an aliquot containing up to 20 μg . of cobalt. Evaporate the solution almost to dryness, add 1 to 2 ml. of concentrated nitric acid, and evaporate to dryness. Dissolve the residue in 10 ml. of water containing 0.5 ml. of 1 : 1 hydrochloric acid and 0.5 ml. of 1 : 10 nitric acid. Boil for a few minutes to ensure complete dissolution. Add 2.0 ml. of nitroso-R salt solution and 2 g. of hydrated sodium acetate. The *pH* should be about 5.5 ; check it with bromocresol green. Boil for a minute, add 1.5 ml. of concentrated hydrochloric acid, boil for another minute, and then cool the solution. Transfer it to a 50 ml. volumetric flask, dilute to volume, mix, and measure the optical density at 510 $\text{m}\mu$ against a reagent blank. Use either a single standard or a calibration curve.

Copper

Copper reacts with dithizone (diphenyl-thiocarbazone) in dilute mineral acid to form a red-violet keto complex. Interference occurs from gold, mercury, palladium, and silver, which react under the same conditions. Bismuth reacts in acid conditions, but small amounts can be tolerated. Ferric iron tends to oxidise dithizone and should be absent. Lead, cadmium, nickel, and zinc may be present in moderate amounts.

The following solutions will be required :—

(1) *Standard Copper Solution*.—Dissolve 0.1000 g. of electrolytic copper in 1 : 1 nitric acid, boil to expel oxides of nitrogen, and dilute to 1 litre. Dilute this stock solution ten-fold to obtain a solution containing 10.0 μ g. of copper per ml.

(2) *Dithizone Solution*.—Dissolve 0.0500 g. of dithizone in 500 ml. of pure carbon tetrachloride, free from any substances that inhibit the copper reaction. Dilute this stock solution ten-fold as required, with pure carbon tetrachloride. Keep the stock solution in a cold, dark place.

(3) *Hydrochloric Acid and Water*.—Redistilled in an all-glass still.

Procedure.—If necessary make a preliminary separation of copper. To do this, carry through the dithizone extraction procedure described below, then wash the carbon tetrachloride extract first with 10 ml. of 2 per cent. potassium iodide solution in 0.1N hydrochloric acid containing a little sodium sulphite and then with 5 ml. of 0.01N hydrochloric acid. This process removes traces of silver, mercury, and bismuth. Evaporate the organic phase to dryness, and heat it with 0.5 ml. of concentrated sulphuric acid and 0.2 ml. of 60 or 70 per cent. perchloric acid to destroy organic matter. Cool the acid solution and dilute it with 10 ml. of water. Almost neutralise the solution with ammonia, and transfer it to a small separating funnel and shake for 2 minutes with 5 ml. of 0.001 per cent. dithizone solution. If the colour of the carbon tetrachloride layer is red add another 5 ml. of reagent to ensure an excess of dithizone. Not more than 5 μ g. of copper should be present if only 5 ml. of reagent are to be used. Separate the layers and measure the optical density of the carbon tetrachloride layer at either 510 $m\mu$ or 625 $m\mu$, using carbon tetrachloride as comparison liquid. Construct a calibration curve for the range 0 to 5.0 μ g. of copper per 5 ml. of solvent. If more than 5 ml. of reagent were used construct a curve for that particular volume.

Lead

Traces of lead are probably best determined by means of dithizone, provided proper precautions are taken. If a basic solution of lead, containing cyanide and citrate or tartrate,

is extracted with a chloroform or carbon tetrachloride solution of dithizone, the lead is completely extracted, and the only other metals extractable in these conditions are bismuth, thallium and stannous tin. However, other difficulties may arise. Ferric iron in more than traces is not permissible since it forms ferricyanide which oxidises dithizone, and it should be reduced, if present, with hydroxylamine hydrochloride. Copper may also cause oxidation. The solution must be free from precipitates such as calcium or magnesium phosphate or stannic acid, which occlude lead. Lead may readily be separated from iron and copper by extraction in basic medium in the absence of cyanide and back-extraction of the lead into an acid medium.

The following solutions will be required :—

(1) *Dithizone Solution A*.—Dissolve 50 mg. of dithizone in 1 litre of chloroform. Store in the dark.

(2) *Dithizone Solution B*.—Dissolve 50 mg. of purified dithizone in 1 litre of redistilled chloroform. Store in the dark.

(3) *Ammonium Hydroxide Solution*.—Prepare a saturated solution from cylinder ammonia as described on p. 514.

(4) *Nitric Acid Solution*.—Dilute concentrated nitric acid, redistilled if necessary, with 100 volumes of water.

(5) *Ammonium Citrate Solution*.—A 50 per cent. solution in water, made just ammoniacal, and freed from lead by extraction with dithizone solution A, and from excess dithizone by extraction with chloroform.

(6) *Potassium Cyanide Solution*.—A 10 per cent. solution in water, freed from lead if necessary by treating a 50 per cent. solution in the manner just described for the citrate solution, and then diluting.

(7) *Hydroxylamine Hydrochloride Solution*.—A 20 per cent. solution in water, freed from lead and other heavy metals if necessary by preparing a more concentrated solution, making it just ammoniacal, adding a few ml. of a 5 per cent. sodium diethyldithiocarbamate solution, extracting with chloroform, reacidifying with hydrochloric acid (use *m*-cresol purple as indicator) and diluting.

(8) *Ammoniacal Cyanide Solution*.—Dissolve 20 g. of potassium cyanide in water, add 150 ml. of concentrated ammonia solution and dilute to 1 litre with water.

(9) *Standard Lead Solution*.—Dissolve 0.160 g. of dried lead nitrate in 100 ml. of water containing a little nitric acid. Dilute 1 ml. of this 0.100 per cent. solution to 100 ml. with 1 : 100 nitric acid to obtain a 0.00100 per cent. lead solution. One ml. of this solution contains 10.0 μ g. of lead.

Procedure.—Take an aliquot of the sample solution, containing 1 to 100 μ g. of lead in a separating funnel, and add to it 15 ml. of ammonium citrate solution and 1 ml. of hydroxylamine hydrochloride solution and a few drops of thymol blue indicator. Add ammonium hydroxide until the solution is basic, and then 5 ml. of potassium cyanide solution. Adjust the *pH* to the green colour of the indicator, add 5 ml. of dithizone solution A and shake for 15 seconds. Separate the organic phase and extract again with 5 ml. of dithizone. Combine the extracts and extract again if necessary (the last extract should show no mixed colour, but only the colour of dithizone). Shake the combined extracts with 20 ml. of water and withdraw the chloroform layer into another separating funnel. Extract the aqueous layer with 1 or 2 ml. of dithizone solution, and add this extract to the others. Shake the chloroform extracts with two 25 ml. portions of the 1 : 100 nitric acid solution. Bismuth, if present, may be removed by adjusting the *pH* of the acid solution to 3.0 (add thymol blue indicator and adjust carefully to the yellow colour of the indicator) and shaking for 2 minutes with 2 to 3 ml. portions of 0.005 per cent. dithizone solution in chloroform. The appearance of an orange or mixed colour indicates the presence of bismuth. Remove any droplets of dithizone solution by extracting with chloroform, and leave the bore of the stopcock filled with chloroform.

To the acid lead solution add 35 ml., accurately measured, of 0.001 per cent. dithizone solution obtained by diluting dithizone solution B with pure chloroform. Add 10.0 ml. of ammoniacal cyanide solution, shake for 1 minute and allow the phases to separate. If the organic phase is red, indicating an insufficiency of dithizone, add another 5 ml. of 0.001 per cent. solution and shake again. Run a small amount of the organic phase through the stem of the funnel to remove the chloroform left in the bore of the stopcock and then fill an absorption cell and cover it to prevent evaporation. Measure the optical density at 510 $m\mu$, using water as reference liquid.

Prepare a calibration curve by treating aliquots of the standard lead solution in the same way as the sample. The optical density of the diluted dithizone solution should be checked to make sure that no change has taken place in the stock solution B since the calibration curve was prepared.

Manganese

Manganese is usually determined colorimetrically by oxidation to permanganate. The reaction is sensitive and specific. Reducing agents must be absent, but this is easily achieved by an initial evaporation with sulphuric acid. If only small amounts of manganese are present it is necessary to ensure the absence of nitrite; nitric acid is often used in the process of preparing the solution, and is best removed by evaporation with sulphuric acid. If periodate is used as the oxidant and iron is present, phosphoric acid should be added to prevent precipitation of ferric periodate. The interference of coloured ions can be eliminated by using an aliquot of unoxidised solution as the reference liquid.

The following solution will be required :—

Standard Manganese Solution.—Dissolve 0.2880 g. of pure potassium permanganate in water, add a little dilute sulphuric acid and a little sodium sulphite (enough to reduce the permanganate) and boil out the sulphur dioxide. Dilute the solution to 1 litre to obtain a solution containing 0.100 mg. of manganese per ml.

Procedure.—If necessary, remove reducing agents and halides by adding nitric and sulphuric acids and evaporating to fumes of sulphuric acid. The solution for analysis should contain 0 to 0.1 mg. of manganese per ml. Transfer a 10 ml. aliquot of sample solution to a 250 ml. conical flask. Dilute the solution to about 70 ml., add 5 ml. of concentrated sulphuric acid and 5 to 10 ml. of syrupy phosphoric acid. Add 0.3 g. of potassium metaperiodate, bring to the boil, with stirring, and keep just below boiling-point for at least 10 minutes. Cool, transfer to a 100 ml. volumetric flask, and dilute to volume. Measure the optical density at 525 m μ . Prepare a calibration curve. Use water or a reagent blank as comparison liquid.

Molybdenum

Sexivalent molybdenum reacts with dithiol (4-methyl-1 : 2-dimercaptobenzene) in dilute mineral acid solution to give a precipitate which can be extracted with butyl acetate to yield a green solution. Many metals are precipitated by the reagent but only a few of the complexes are soluble in butyl acetate. Small amounts of copper, iron, and tin do not interfere. Tungsten behaves similarly to molybdenum, but its interference can be prevented by addition of citric acid. Beer's law is obeyed.

The following solutions will be required :—

(1) *Standard Molybdenum Solution*.—Dissolve 0.1500 g. of molybdenum trioxide in a few ml. of dilute sodium hydroxide, make slightly acid with hydrochloric acid, and dilute to 1 litre. One ml. of this solution contains 0.100 mg. of molybdenum.

(2) *Dithiol Solution*.—Add 0.1 g. of dithiol to 100 ml. of 0.25N sodium hydroxide. Add 0.5 ml. of thioglycollic acid to the solution. This solution must be freshly prepared.

(3) *Butyl Acetate*.—Redistilled.

Procedure.—Transfer a 10 ml. aliquot of sample, containing from 1 to 25 μ g of molybdenum, to a beaker, dilute it to 20 ml., add 2 ml. of dithiol solution, and allow to stand for 2 hours. Extract the molybdenum complex with two portions, 14 ml. and 9 ml., of butyl acetate. Dilute the combined extracts to 25 ml. with butyl acetate and determine the optical density at 670 m μ , using butyl acetate as reference liquid. Prepare a calibration curve, using an appropriate dilution of the standard molybdenum solution.

Nickel

When dimethylglyoxime is added to a basic solution of a nickel salt that has been treated with an oxidant such as bromine, a wine-red or brown colour is produced. The particular colour obtained depends on the original acidity of the nickel solution. The nature of the complex formed is not known. Beer's law is obeyed but the intensity of colour is not constant ; the rate of change of intensity with time depends on the wavelength used for measurement and on the experimental conditions. Copper and cobalt give colours with the reagent but do not interfere unless present in amounts greater than that of

the nickel. Interference from iron, aluminium, etc., can be prevented by adding citric acid. Chromium may cause high results. It is usual to make a preliminary extraction of the nickel to eliminate interferences.

The following solutions will be required :—

(1) *Standard Nickel Solution*.—Dissolve 0.673 g. of nickel ammonium sulphate in water, and dilute the solution to 1 litre. Dilute a portion of this solution ten-fold to obtain a solution containing 10.0 μ g. of nickel per ml.

(2) *Dimethylglyoxime Solution*.—Dissolve 1 g. in 100 ml. of ethanol.

(3) *Sodium Citrate Solution*.—Dissolve 10 g. in 100 ml. of water.

(4) *Bromine Water*.—Prepare a saturated solution.

Procedure.—Prepare the sample solution so that it is slightly acid and contains from 1 to 15 μ g. of nickel per ml. Transfer a 10 ml. aliquot of sample solution to a separating funnel. Add 5 ml. of sodium citrate solution and make slightly ammoniacal. Add 2 ml. (more if much cobalt is present) of dimethylglyoxime solution. Extract with three 2 to 3 ml. portions of chloroform. Wash the combined extracts with 5 ml. of 1 : 50 ammonia and collect the chloroform layer. Shake the chloroform extracts vigorously with two 5 ml. portions of 0.5N hydrochloric acid. Transfer the aqueous phase to a 25 ml. volumetric flask. Add 10 drops of bromine water to the solution, and then ammonia until the bromine colour disappears. Add 1 ml. of concentrated ammonia solution. Cool the solution to less than 30° and add 1 ml. of dimethylglyoxime solution. Dilute to volume and determine the optical density at 540 m μ within 5 minutes, using a reagent blank as reference liquid. A standard solution should be run and should have about the same initial acidity as the sample.

Phosphorus

Phosphorus is usually determined colorimetrically by forming the heteropoly acid, phosphomolybdic acid, and reducing this to form the substance known as molybdenum blue. Many reductants have been proposed in the literature. The main interferences are from other substances, such as silicon, arsenic, and germanium, which also form heteropoly acids.

A method that is less subject to interference involves the formation of the mixed heteropoly acid, phosphovanado-molybdc acid. The main interfering ions are fluoride, iodide, permanganate, chromium, thorium, and platinum. Beer's law is obeyed.

The following solutions will be required :—

(1) *Standard Phosphorus Solution*.—Dissolve 0.4387 g. of potassium dihydrogen phosphate in water and dilute to 1 litre. Dilute this stock solution ten-fold to obtain a solution containing 10.0 μ g. of phosphorus per ml.

(2) *Nitric Acid Solution*.—Add 200 ml. of concentrated nitric acid to 400 ml. of water.

(3) *Ammonium Vanadate Solution*.—Dissolve 0.25 g. of ammonium metavanadate in water and dilute to 100 ml.

(4) *Ammonium Molybdate Solution*.—Dissolve 5 g. of ammonium molybdate in water and dilute to 100 ml. Store in a plastic bottle.

Procedure.—Transfer an aliquot of sample, containing between 0.1 and 5 mg. of phosphorus, to a 100 ml. volumetric flask. Add 10 ml. of nitric acid solution, 10 ml. of ammonium vanadate solution, and 10 ml. of ammonium molybdate solution in that order, mixing between additions. Dilute to volume, and measure the optical density at 470 m μ , using a reagent blank as comparison liquid. Construct a calibration curve or run a standard.

Silicon

Silicon is usually determined colorimetrically by forming silicomolybdc acid and reducing it to form molybdenum blue. Interference from phosphorus can be eliminated by adding citric or tartaric acid before the reduction. Interference from other elements which form heteropoly acids can be eliminated by solvent extraction methods.

The following solutions will be required :—

(1) *Standard Silicon Solution*.—Fuse 0.2140 g. of pure quartz with 1 g. of purest sodium carbonate, in a platinum crucible. Dissolve the melt in water and dilute to 1 litre. Store in a plastic bottle. Dilute this solution ten-fold, as required, to obtain a solution containing 10.0 μ g. of silicon per ml.

(2) *Ammonium Molybdate Solution*.—Dissolve 75 g. of ammonium molybdate in 750 ml. of water. Add 100 ml. of 1 : 1 sulphuric acid and dilute to 1 litre with water. Store in a plastic bottle.

(3) *Reducing Solution*.—Dissolve 7 g. of sodium sulphite in water. Add 1.5 g. of 1-amino-2-naphthol-4-sulphonic acid and stir until dissolved. Dissolve 90 g. of sodium bisulphite in 800 ml. of water and mix the solution with the sodium sulphite solution. This solution slowly deteriorates.

(4) *Tartaric Acid Solution*.—Dissolve 10 g. of tartaric acid in a litre of water. Store in a plastic bottle.

Procedure.—Prepare the sample solution so that it contains up to 10 μg . of silicon per ml. and is slightly acid. Transfer 50 ml. of sample solution to a 100 ml. volumetric flask. Add 1 ml. of the ammonium molybdate solution, mix, and allow to stand for at least 10 minutes. Add 4 ml. of the tartaric acid solution and 1 ml. of the reducing solution, mixing between additions. Dilute to volume and allow to stand for at least 30 minutes. Determine the optical density at 650 $\text{m}\mu$ using a reagent blank as reference liquid. Run a standard with 50 ml. of the standard silicon solution. Arsenic and germanium must be absent from the sample solution.

Titanium

Titanium is generally determined colorimetrically by means of the brownish-yellow colour developed when quadrivalent titanium reacts with hydrogen peroxide. The reaction is usually carried out in sulphuric acid solution. Interference is caused by vanadium and molybdenum, which give yellow colours with the reagent, and hexivalent chromium which gives a blue colour. It is possible to extract the chromium compound with ethyl acetate. The effect of vanadium and molybdenum can be overcome by measuring the absorption at the wavelengths of maximum absorption for these elements (460 and 330 $\text{m}\mu$ respectively) and applying an appropriate correction. Fluoride and phosphate interfere by forming stable complexes with the titanium. The effect of phosphate varies with the wavelength used for the absorption measurement. At 400 $\text{m}\mu$ the effect is least. Phosphoric acid is often added to form a complex with ferric iron, since the yellow colour of the ferric

solution interferes in the determination. Large amounts of alkali sulphates have a slight bleaching effect. The standard solutions used should contain the same amounts of phosphoric acid and alkali sulphates as do the sample solutions.

The following solutions will be required :—

(1) *Standard Titanium Solution*.—Weigh 0.5013 g. of pure dry potassium titanium fluoride K_2TiF_6 into a platinum crucible. Add concentrated sulphuric acid and evaporate (Fig. 13, p. 37) almost to dryness. Repeat this operation several times until the hydrofluoric acid is completely expelled. Dissolve the residue in a little sulphuric acid and dilute with 5 per cent. sulphuric acid to 250 ml. One ml. of the solution contains 0.500 mg. of titanium.

(2) *Sulphuric Acid Solution*.—Dilute 30 ml. of the concentrated acid to 1 litre to obtain a 5 per cent. w/w solution.

(3) *Hydrogen Peroxide*.—A 3 per cent. solution.

Procedure.—Transfer an aliquot of sample solution, containing up to 2.5 mg. of titanium, to a 100 ml. volumetric flask. If iron is present add dilute phosphoric acid from a burette until the iron colour is discharged. Add the same amount to the reagent blank and the standards. Add 5 ml. of hydrogen peroxide solution, and dilute to volume with 5 per cent. sulphuric acid. Measure the optical density at 400 $m\mu$, using a reagent blank as comparison liquid. Construct a calibration curve or run a single standard.

COLORIMETRIC DETERMINATION OF THE *pH* OF A LIQUID BY MEANS OF INDICATORS

It has already been pointed out that indicators undergo a change in colour when a marked alteration occurs in the *pH* value of a solution containing them (p. 78). Use may also be made of them for the actual determination of *pH*, as an alternative to an electrometric method described in Part II.

An approximate determination of the *pH* of the liquid is made by using a mixture of indicators so chosen that a series of different colours is given over a wide range of *pH* values. A specified amount of the mixture is added to a definite volume of the solution to be tested, and by reference to a colour chart

the pH may be judged to about 0.5 of a unit.¹ This may be sufficiently accurate in many cases, but if a more exact determination is required, special solutions must be prepared, mixtures of which have pH values including the approximate value of pH found. An indicator must then be selected whose range of colour change also contains this pH value. The preparation of these solutions, known as "buffer" solutions,² and lists of indicators with their pH ranges will be found in books dealing specifically with the measurement of hydrogen ion concentration. A universal buffer may be obtained from dealers by means of which solutions of any pH value between 2.7 and 11.4 may be prepared by simple addition of the requisite amount of standard acid or alkali.

As an example of the procedure to be adopted, a method for determining the pH when this lies between 5 and 8 is here described.

Determination of pH between the Values 5 and 8

The following solutions are required :—

(1) *Disodium Hydrogen Phosphate*.—Dissolve 23.88 grams of $Na_2HPO_4 \cdot 12H_2O$ in water, and dilute to 1 litre. "Chemically pure" crystals, free from efflorescence, are satisfactory. The pH of this solution is 9.2.

(2) *Potassium Dihydrogen Phosphate*.—Dissolve 9.08 grams of KH_2PO_4 in water, and dilute to 1 litre. The salt must be free from chloride and sulphate. The pH of this solution is 4.5.

¹ Such a mixture and colour chart may be obtained from chemical dealers.

² A buffer solution is one whose pH is not appreciably altered by the addition of considerable amounts of acids or alkalis. Such a solution is formed when a weak acid, for example acetic acid, is added to a solution of one of its salts, say sodium acetate. The liquid will contain a large amount of acetate ions, which will combine with any hydrogen ions added, forming unionised acetic acid; and it also contains a considerable amount of unionised acetic acid, which will provide hydrogen ions to combine with any hydroxyl ions added. In this way any fall or rise in pH is hindered. The addition of a salt such as potassium dihydrogen phosphate, KH_2PO_4 , will also buffer an aqueous solution; for the $H_2PO_4^-$ ions will take up added hydrogen ions to give unionised H_3PO_4 , and also provide hydrogen ions to neutralise hydroxyl ions added.

Suitable indicators for the *p*H range 5 to 8 are :—

Indicator.	<i>p</i> H range.	Colour change.	Concentration of solution.
Methyl red . .	4·4 – 6·2	Red—yellow	0·1% in 60% alcohol
Bromo-cresol purple .	5·2 – 6·8	Yellow—purple	0·05% in 20% alcohol
Bromo-thymol blue .	6·0 – 7·6	Yellow—blue	0·05% in 20% alcohol
Phenol red . .	6·8 – 8·4	Yellow—red	0·05% in 20% alcohol

Procedure.—Measure 50 ml. of the solution to be tested into a Nessler tube, and add 1 ml. of the appropriate indicator selected from the above list. Into a second Nessler tube, measure 25 ml. of the potassium dihydrogen phosphate, or of the disodium hydrogen phosphate, selecting that solution which must be in excess, as shown by the tables below. Add 1 ml. of the indicator, and run in from a burette the other phosphate solution until an approximate match in colour is obtained. Read the volume added and reject the liquid. Prepare a fresh standard, taking proportional amounts of the two phosphate solutions such that the total volume will be approximately 50 ml., add the indicator, and make the final adjustment by addition of one or other of the phosphate solutions as required to obtain an exact match. The *p*H may then be found by reference to the tables.

TABLE I.

(*p*H 5 – 6·8).

Volume of KH_2PO_4 solution taken
= 25 ml.

Volume of Na_2HPO_4 solution added.	<i>p</i> H.
0·3	5·0
0·6	5·3
1·7	5·7
2·2	5·8
3·6	6·0
4·5	6·1
6·1	6·2
7·3	6·3
9·2	6·4
12·3	6·5
15·2	6·6
19·2	6·7
24·2	6·8

TABLE II.

(*p*H 6·9 – 8).

Volume of Na_2HPO_4 solution taken
= 25 ml.

Volume of KH_2PO_4 solution added.	<i>p</i> H.
19·1	6·9
15·8	7·0
12·9	7·1
9·3	7·2
7·2	7·3
5·6	7·4
4·5	7·5
3·7	7·6
3·15	7·7
2·35	7·8
1·8	7·9
1·4	8·0

Procedure in the Case of a Slightly Coloured Liquid.—

In this case, it is necessary to compensate for the colour of the liquid by matching the solutions in 50 ml. Nessler tubes, arranged as shown in Fig. 64. The light that illuminates the

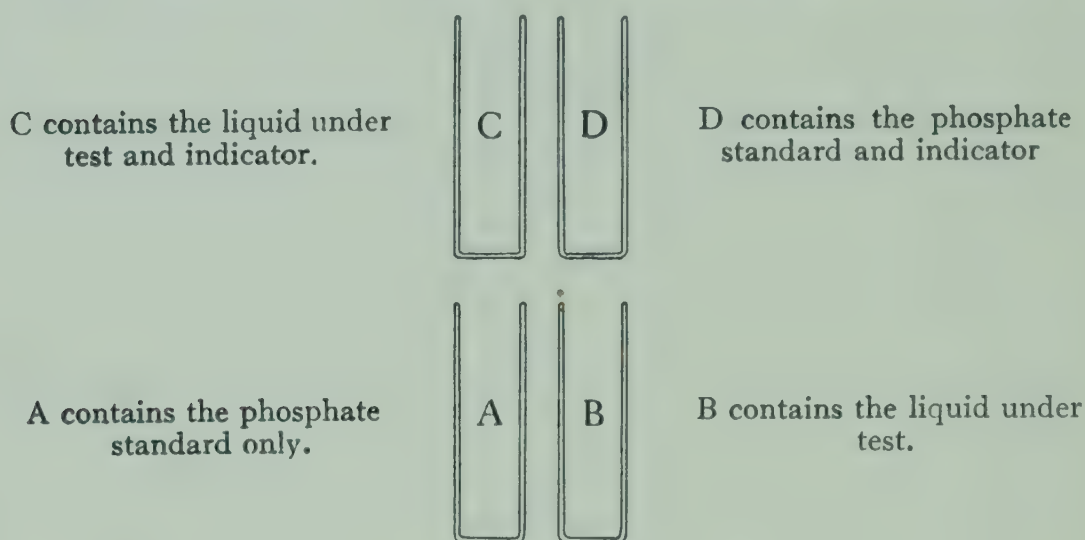


FIG. 64.

phosphate standard in D is made to pass also through the tube B containing the liquid under test (without indicator), whilst the light that reaches the eye through the liquid under test (with indicator) in C passes also through a column of phosphate standard in A.

DETERMINATION OF TRACES OF ARSENIC BY A MODIFIED GUTZEIT METHOD

The following method may be used for the detection and estimation of small quantities of arsenious oxide, the least amount that can be estimated being of the order of 0.001 mg. The arsenic is converted to arsine, which gives, on discs of filter paper impregnated with mercuric chloride, a yellow stain with small amounts of arsine, changing to brown as the amount of arsine increases. The stain obtained is compared with a series of stains produced by the use of known amounts of arsenic. The reduction to arsine is effected by nascent hydrogen generated electrolytically (preferably on a mercury cathode), or more simply by the action of hydrochloric acid on "arsenic-free" zinc. The stains may be intensified and made permanent by soaking the discs in a solution of potassium iodide.

The following materials are required :—

(1) *Standard Arsenic Solution*.—Weigh out 0.0500 gram of pure arsenious oxide into a small beaker, and dissolve it in

a few millilitres of dilute sodium hydroxide solution. Acidify the solution with hydrochloric acid, and make up to 1 litre in a standard flask. Dilute 10 ml. of this solution to 250 ml. in another standard flask. One ml. of this last solution contains 2.00 mg. of As_2O_3 .

(2) *Lead Acetate Papers*.—Cut several pieces of filter paper 10 by 5 cm., and soak them in a 10 per cent. solution of lead acetate in recently boiled water. Dry the papers, and keep them in a closed tube.

(3) *Mercuric Chloride Papers*.—Cut several strips of filter paper 2.5 cm. in width, and soak them in a saturated solution of mercuric chloride. Place them on a dry filter paper to remove excess liquid, and dry them at about 60° in the dark. Keep these in a closed tube in the dark.

Procedure.—Fit a wide-mouthed bottle of 110 to 120 ml. capacity with a rubber stopper through which is passed a glass tube 20 cm. in length, and 6.5 mm. in internal diameter. One end of the glass tube must have been drawn out to a diameter of about 1 mm., and a hole blown in the side of the tube as near to this end as possible. The tube is inserted so that the hole is just below the lower surface of the stopper. Care must be taken to see that the constricted end of the tube will be above the level of the liquid in the bottle when about 70 ml. have been added. Carefully bore holes of 6.5 mm. diameter as nearly centrally as possible through two rubber stoppers of 2.5 cm. diameter at the wider end, the boring being started at the wider ends. Insert the upper end of the glass tube, which must have been previously ground flat on a fine carborundum stone, into one of the rubber stoppers so that the ground end of the tube is flush with the wider end of the stopper. Roll up one of the prepared lead acetate papers in the form of a cylinder 10 cm. in length, and place it inside the glass tube so that the upper end is not less than 2.5 cm. below the top of the tube. This paper serves to remove any hydrogen sulphide which would



FIG. 65.—Apparatus for determining arsenic.

produce a stain on the mercuric chloride paper. Cut a disc of 2.5 cm. diameter from a piece of the mercuric chloride paper, and place it on the rubber stopper centrally over the glass tube. Attach the other rubber stopper with the wide end downwards, so that the holes in the two stoppers are in line, by means of two strong rubber bands. This arrangement ensures that the gas generated in the bottle will pass through the disc.

Prepare a series of standards as follows :—Place 10 grams of “arsenic test” zinc in the bottle, and add a few small crystals of stannous chloride. Add 2 ml. of the standard arsenic solution, and then approximately 60 ml. of 2N hydrochloric acid (free from arsenic), and at once insert the stopper with the tube fitted as above. Place the bottle in a large beaker or jar containing water at room temperature, and allow the reaction to proceed for an hour. Remove the mercuric chloride paper disc, and immerse it in a 10 per cent. solution of potassium iodide until the red colour of mercuric iodide at first produced disappears, leaving a brown stain. Allow the disc to dry in the dark on a sheet of filter paper, and number it when dry. Repeat the procedure, increasing the amount of arsenic solution used by 2 ml. each time, and using fresh mercuric chloride and lead acetate papers, and fresh zinc and hydrochloric acid. A series of five discs thus prepared will be sufficient.

If the arsenic content of the liquid to be investigated is entirely unknown, a preliminary test must be carried out starting with one millilitre of the solution, and examining the stain at the end of 15 minutes. If this is not clearly within the range of standards, fresh tests must be made with different amounts of the unknown solution, the hydrochloric acid and zinc being renewed when necessary. When a suitable amount of the unknown arsenic solution has been decided upon, the actual determination must be carried out exactly as described for the preparation of the standards.

SUGGESTED READING

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PART V

SYSTEMATIC QUANTITATIVE ANALYSIS

ALUMINIUM

IN the analysis of a complex mixture, iron and aluminium are usually separated together from all other metals before separation from one another, and are generally obtained finally as a mixture of ferric oxide and alumina. The iron in the mixed oxides may be determined volumetrically and the aluminium found by difference or determined by any suitable method.

Aluminium may also be determined volumetrically (pp. 105, 317), and colorimetrically (p. 294).

Forms in which Aluminium is precipitated

Aluminium Hydroxide.—This is the easiest method for the determination of aluminium, but is limited in applicability on account of the general insolubility of metallic hydroxides. For details of the procedure, see p. 254.

Basic Aluminium Acetate.—The method serves to separate aluminium, iron and titanium (but not chromium) from nickel, cobalt, manganese, zinc, calcium, and magnesium. It depends on the fact that the acetates of the trivalent metals hydrolyse in hot solution more than do those of the bivalent metals.

Aluminium Phosphate.—This method is of special value for the separation of aluminium from iron.

Aluminium Oxinate.—By the use of this method aluminium may also be determined volumetrically.

Basic Aluminium Benzoate.—By this method iron, aluminium, titanium, zirconium, and chromium may be separated from manganese, calcium, barium, strontium, cobalt, nickel, and magnesium. Phosphate does not interfere, neither chromium nor aluminium phosphate being precipitated. The presence of benzoate in the filtrate does not affect the subsequent determination of the alkaline earth metals. The amount of material coprecipitated is negligible.

Determination of Aluminium (and Iron) by the Basic Acetate Method

OUTLINE OF METHOD.—The solution is neutralised and diluted. Ammonium acetate is added and the solution boiled, whereby basic aluminium and ferric acetates are precipitated. After a second precipitation by ammonia, the precipitate is ignited and the mixture of Fe_2O_3 and Al_2O_3 is weighed. The Fe_2O_3 in the mixed oxides is then determined and the Al_2O_3 found by difference.

Basic Aluminium Acetate is a bulky, gelatinous precipitate, insoluble in water or in slightly alkaline solutions. It probably varies considerably in composition according to the method of preparation. Unless precipitated under the exact conditions given below, it forms a jelly-like mass which cannot be filtered satisfactorily. It is readily soluble in all acids. It occludes to some extent all soluble salts that may be present in the solution, and these cannot be completely removed by washing. If washed with water, it becomes more gelatinous and chokes the pores of the filter.

On ignition it is completely converted into Al_2O_3 , but if the solution contained alkali salts, the precipitated basic acetate is contaminated with occluded alkali salts, and the oxide obtained is also impure.

Basic Ferric Acetate corresponds closely in properties with the aluminium salt, but is less soluble in acetic acid.

Procedure.—The basic acetate method is never used unless it is necessary to separate iron and aluminium from other metals. In the following description of the method it is therefore assumed that a separation of iron and aluminium from other metals, such as manganese, is desired.

Concentrate the slightly acid solution, which should contain not more than 0.1 gram of either metal as chloride, in a small beaker to about 10 ml. After cooling, transfer the solution to a 600 ml. beaker and add dilute ammonia cautiously, with constant stirring, until a slight permanent precipitate is produced. Then add dilute hydrochloric acid, drop by drop, stirring for some time after each drop, until the precipitate is just redissolved. Unless the amount of iron is small, the solution at this stage should be clear brown in colour; if it is yellow, too much acid has been added. Add 2 grams of sodium acetate dissolved in a little water. If the conditions have been correctly observed, no precipitate will form at this

stage, but the solution will become darker and redder in colour. Dilute with boiling water to about 350 ml., and boil briskly for *not more than two minutes*. Allow the precipitate to settle for a short time only, and filter as rapidly as possible through an ashless filter paper, using slight suction produced by a looped suction tube (Fig. 19, p. 45). If the solution is boiled for more than two minutes, or is allowed to cool before filtration, the precipitate becomes so gelatinous that filtration is almost impossible. If aluminium is the only trivalent metal present, the light precipitate formed settles slowly, and filtration is therefore more difficult than is the case when a considerable proportion of iron is present.

The precipitate is mainly basic ferric and aluminium acetates, but contains also occluded salts. Wash twice with hot water and then redissolve the precipitate by pouring hot dilute nitric acid on it without removal from the filter paper. Wash the paper once with hot dilute nitric acid and then with hot water. Add 2 ml. of concentrated nitric acid to the solution, and reprecipitate with a slight excess of ammonia. Heat until boiling, filter through the same filter paper, and wash thoroughly with hot water. (Combine the two filtrates for the determination of manganese, etc.)

Incinerate the filter paper together with the precipitate in a platinum crucible without previous drying, ignite over a Méker burner, and weigh the mixture of ferric oxide and alumina.

Fuse the mixed oxides with potassium pyrosulphate (p. 439), determine the iron volumetrically, and calculate the weight of ferric oxide equivalent to it. The difference between this and the weight of the mixed oxides is the weight of the alumina.

Determination of Aluminium as Aluminium Phosphate and its separation from Iron

OUTLINE OF METHOD.—The aluminium is precipitated in presence of acetic acid by boiling the solution with sodium phosphate and sodium thiosulphate. The precipitate is ignited, and is weighed as AlPO_4 . The iron in the filtrate is precipitated as sulphide, converted to hydroxide, and weighed as Fe_2O_3 .

Procedure.—To the acid solution (which should not contain more than 50 mg. of aluminium, and may also contain iron), add about 2 gm. of sodium phosphate, and then

ammonium carbonate until a permanent precipitate is obtained. Redissolve the precipitate in dilute hydrochloric acid and add 1 ml. in excess. Dilute the solution to about 300 ml., add about 5 grams of sodium thiosulphate, heat until boiling, and add 20 ml. of dilute acetic acid. Boil for twenty minutes in order to coagulate the precipitated sulphur and to reduce the iron to the ferrous condition. (Ferrous phosphate is not precipitated in presence of acetic acid.)

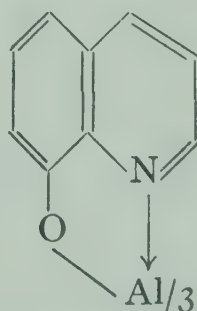
Filter off, and wash with hot water. Dry the precipitate (partially at least) and incinerate the filter together with the precipitate. Ignite and weigh the aluminium phosphate obtained.

If iron is to be determined in the filtrate, evaporate to about 150 ml., and precipitate the iron by the addition of a slight excess of ammonium sulphide. Filter, and wash the ferrous sulphide thoroughly with a dilute solution of ammonium sulphide to prevent oxidation. Dissolve the precipitate on the filter with hot dilute hydrochloric acid, and wash the filter with hot water. To recover traces of iron ignite the filter paper, and after the carbon has burned away extract the ash with a little warm concentrated hydrochloric acid; dilute, filter through a small filter paper, and add the filtrate to the main iron solution. Boil to expel hydrogen sulphide, oxidise with nitric acid, precipitate the iron as ferric hydroxide, and weigh as ferric oxide as described on p. 251.

Iron may also be separated from aluminium by precipitation with cupferron as described on p. 250.

Determination of Aluminium by Means of Oxine

Oxine, 8-hydroxyquinoline, C_9H_7ON , gives sparingly soluble precipitates under suitable conditions with many metals, the hydrogen of the hydroxyl group being replaced and a chelate ring formed, *e.g.*



The precipitates are easily filtered off, and if dried at definite temperatures are of constant composition. Although the reagent

is not specific, by adjustment of the pH of the solution certain metals may be separated quantitatively from mixtures containing them.

Alternatively, the metal may be indirectly determined by a volumetric method, the precipitate being decomposed by hydrochloric acid, and the oxine titrated by means of a standard bromate-bromide solution.

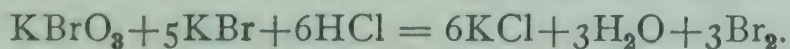
Procedure.—Weigh accurately an amount of alum which does not contain more than 0.03 gram of aluminium. Dissolve this in about 100 ml. of water in a 250 ml. beaker. Heat almost to boiling, clear the solution if necessary by the cautious addition of two or three drops of dilute sulphuric acid, and run in from a burette an excess of a solution of the reagent prepared by warming 2.5 grams of oxine with 4 ml. of glacial acetic acid and 10 ml. of water, and finally diluting to 100 ml. One ml. of this solution must be added for each 1.6 mg. of aluminium present, and then 10 ml. in excess. (See Miller and Chalmers, *Analyst*, 1953, **78**, 686.) If a precipitate appears, just redissolve it with 0.1N hydrochloric acid. If no precipitate appears, add dilute ammonia until one does, and then redissolve it with 0.1N hydrochloric acid. Heat the solution to boiling, and add dropwise, with constant vigorous stirring, a 2N solution of ammonium acetate until a precipitate appears, and then a further 30 ml. of the 2N ammonium acetate at the same rate and with continuous stirring. Digest the precipitate for 5 minutes and then filter it off on a No. 4 porosity sintered glass crucible. Wash the filter and precipitate with hot water, dry them at 150° , cool, and weigh. The precipitate has the composition $Al(C_9H_6ON)_3$.

The precipitate need not be dried if the aluminium is determined indirectly by the following volumetric method.

When oxinates are dissolved in hydrochloric acid, free oxine is formed, which will react with bromine in accordance with the following equation :—



Instead of titrating with a standard solution of bromine, it is better to use a mixture of potassium bromate with excess of potassium bromide which in the acid solution reacts as follows—



From the volume of standard bromate used the amount of oxine and therefore the weight of metal present can be calculated.

The standard solution of potassium bromate, which should be decinormal with respect to the bromine liberated, is prepared by dissolving 0.6959 gram of potassium bromate (M.W./240) together with 3 grams of potassium bromide in water, and making up to 250 ml.

The presence of free bromine showing the end-point of the titration may be indicated by the change in colour of indigo carmine, but it is far more satisfactory to run in a slight excess of the standard bromate-bromide solution, and determine this excess by adding potassium iodide and titrating with thio-sulphate the iodine liberated.

Dissolve the precipitate by pouring warm 6N hydrochloric acid through the crucible, stirring with a short glass rod until dissolution is complete, and wash thoroughly with the warm acid, using in all about 75 ml. Cool, and make up to 100 ml. in a graduated flask.

Displace the air from a 300 ml. conical flask by putting into it 2 grams of sodium bicarbonate, and adding 25 ml. of dilute hydrochloric acid. To this add a measured volume of the oxinate solution containing not more than 0.01 gram of aluminium, and run in the potassium bromate-bromide solution from a burette until, *after standing for a few minutes*, a drop removed by a glass rod gives a blue colour with starch-potassium iodide paper (p. 176). When this is the case, note the volume of the bromate solution which has been added. Add 1 gram of potassium iodide, and titrate the iodine liberated by the excess of bromine with N/10 sodium thiosulphate, adding starch rather earlier than usual since the colour of the solution at the end-point is distinctly yellow. Repeat the titration using an excess of only about 1 ml. of the bromate-bromide solution, as a larger excess may result in the loss of bromine. Deduct the volume of the bromate solution equivalent to the thiosulphate used from the volume originally run in, and calculate the aluminium. One ml. of bromate solution is equivalent to 0.2248 mg. of aluminium.

Other Methods

For the basic benzoate method see Kolthoff, Stenger, and Moskovitz, *J. Amer. Chem. Soc.*, 1934, 56, 812.

For various direct methods for the determination of aluminium in complex mixtures see Kassner and Ozier, *J. Amer.*

Ceram. Soc., 1950, **33**, 250; Hecht, *Mikrochim. Acta*, 1937, **2**, 188; Miller and Chalmers, *Analyst*, 1953, **78**, 686; Chemical Analysis Sub-Committee of the British Ceramic Research Association, *Trans. Brit. Ceram. Soc.*, 1952, **51**, 438.

For a volumetric determination with EDTA see Milner and Woodhead, *Analyst*, 1954, **79**, 363.

AMMONIUM

Ammonia, whether as free ammonia or as an ammonium salt, is determined volumetrically. For details, see pp. 106 and 107.

Traces of ammonia may be determined colorimetrically by means of Nessler's reagent (*Chem. Zentr.*, 1856, **27**, N.F.I. 529).

ANTIMONY

On account of their comparative simplicity and greater accuracy, volumetric methods for the determination of antimony (see pp. 128, 169, and 180) are preferable to any gravimetric method. The bromate method (p. 180) is applicable to mixtures containing antimony, tin, and arsenic.

Traces of antimony may be determined colorimetrically; see p. 295.

The gravimetric determination of antimony is a matter of some difficulty, since in ordinary practice the problem involves the separation of antimony from other elements such as arsenic, with similar chemical properties.

In the analysis of a complex mixture, antimony is usually precipitated as sulphide, together with other metals of the copper and arsenic group.

Antimony Sulphide.—From a hot solution of an antimonious salt, hydrogen sulphide precipitates an orange precipitate of antimonious sulphide which is often contaminated with pentasulphide or with free sulphur.

Antimony sulphide is readily soluble in alkali hydroxides or sulphides, and in ammonium sulphide. The solubility is inappreciable in cold hydrochloric or sulphuric acid (saturated with hydrogen sulphide) up to about 4N solution. No antimony is precipitated by hydrogen sulphide from a 7N hydrochloric acid solution, and a complete separation from arsenic may be obtained by precipitating the arsenic from a strongly acid

solution (two-thirds concentrated hydrochloric acid, by volume) to which about 3 grams of tartaric acid have been added. The arsenic sulphide is filtered and washed with hydrochloric acid (2 : 1). The antimony sulphide is then precipitated by diluting the filtrate with double its volume of warm water and again saturating with hydrogen sulphide. The precipitate is allowed to settle; the supernatant liquid is filtered through a hardened paper, and the precipitate is washed by decantation with dilute acetic acid containing hydrogen sulphide. The filter paper is then opened out on the concave side of a clock-glass, and the sulphide is rinsed from it, into the beaker containing the main part of the precipitate, with hydrochloric acid (2 : 1) in which some potassium chlorate has been dissolved. The contents of the beaker are heated until the precipitate has dissolved, and, after expulsion of chlorine, the antimony is determined volumetrically.

ARSENIC

Arsenic may be determined volumetrically as described on pp. 168 and 181. A colorimetric method is described on p. 310.

Forms in which Arsenic is precipitated

Arsenic Sulphide.—This method gives accurate results if all the arsenic is in the quinquevalent state. The solution, cooled in ice, should be slowly diluted with twice its volume of concentrated hydrochloric acid and saturated with hydrogen sulphide. After collection on a Gooch or sintered glass crucible, the precipitate should be washed with water, dried at 105° to 110° , and weighed as As_2S_5 .

Magnesium Ammonium Arsenate.—The arsenic must be present as arsenate.

Determination as Magnesium Ammonium Arsenate

OUTLINE OF METHOD.—The arsenic is precipitated by “magnesia mixture” in presence of a large excess of ammonia, dried at 110° , and weighed as $\text{MgNH}_4\text{AsO}_4$.

Magnesium Ammonium Arsenate is a white, crystalline precipitate, slightly soluble in water and somewhat less soluble in ammonia solution. The precipitated salt contains six molecules of water of crystallisation, and cannot be completely

dehydrated at 100° . At 110° , it quickly becomes anhydrous, and at somewhat higher temperatures begins to decompose. On ignition, it is converted into magnesium pyroarsenate which, however, decomposes slightly and loses weight if the temperature is very high.

The following solution is required for the precipitation :—*Magnesia Mixture*.—Dissolve 6 grams of magnesium chloride and 7 grams of ammonium chloride in water, add 10 ml. of concentrated ammonia, and dilute to 100 ml.

Procedure.—Evaporate the arsenate solution to 100 ml. and add 1 gram of ammonium chloride. Run in, drop by drop, 20 ml. of magnesia mixture, stirring briskly, but without touching the beaker with the stirring-rod. Then add 15 ml. of concentrated ammonia and set aside for twelve hours. Decant through a Gooch or fine sintered glass crucible, and transfer the precipitate to the crucible with the help of a dilute solution of ammonia (25 ml. of 2N ammonia diluted to 100 ml.) washing the precipitate until the filtrate is free from chloride. Avoid over-washing, as the precipitate is appreciably soluble in dilute ammonia. Place the crucible in the air-oven and raise the temperature slowly, drying finally at 110° to 115° until the crucible reaches constant weight.

BARIUM

Barium may be determined volumetrically as described on pp. 99 and 200.

Forms in which Barium is precipitated

Barium Sulphate.—This is the usual method, and serves for the separation of barium from almost all other metals.

Barium Chromate.—This method is also convenient and accurate. Barium may be separated from strontium by precipitation as chromate from a solution acidified with acetic acid.

Determination of Barium as Sulphate

The solution is made slightly acid with hydrochloric acid, heated until boiling, and the barium precipitated by a hot dilute solution of sulphuric acid. In all other respects the procedure is identical with that adopted for the determination of sulphate (see p. 260).

Determination of Barium as Chromate

OUTLINE OF METHOD.—The barium is precipitated from neutral or slightly acid solution by ammonium chromate. The barium chromate is collected on a Gooch or sintered glass crucible, washed with hot water, dried, and weighed as BaCrO_4 .

Barium Chromate is a yellow, finely divided precipitate which is very slightly soluble in water. At 18° , 1 litre of water dissolves about 4 mg., and the solubility is greater at higher temperatures. It is much less soluble in a dilute ammonium chromate solution. It is appreciably soluble in dilute acetic acid and readily soluble in mineral acids. It can be dried completely at 100° , and may be heated to a red heat without decomposition. If it is heated with organic matter, partial reduction occurs with formation of green chromic oxide; on further ignition with free access of air this is reconverted into chromate.

Procedure.—Neutralise the solution with ammonia or hydrochloric acid, add 1 ml. of acetic acid, and dilute to about 150 ml. Heat the solution until boiling, and precipitate the barium with a hot, dilute solution of ammonium chromate,¹ added through a dropping-tube (p. 261). Place the beaker on the steam-bath until the precipitate settles. Allow to cool. Filter through a Gooch crucible or sintered glass crucible, porosity 4. Rinse the beaker, and transfer the precipitate to the crucible with a dilute (0.2 per cent.) solution of ammonium chromate. Wash finally with cold water until the filtrate is free from chromate.

Place the crucible inside a nickel crucible and heat with a small flame until the precipitate has a uniform yellow colour. Weigh the BaCrO_4 obtained.

BICARBONATE

Bicarbonate may be determined volumetrically (p. 102), or gravimetrically (p. 328).

BISMUTH

In the preparation of a solution for analysis it is advisable, if possible, to use nitric acid in preference to hydrochloric or

¹ Dissolve 1.25 gram of ammonium dichromate (free from sulphate) in 100 ml. of water and add sufficient dilute ammonia—about 5 ml.—to give a lemon-yellow coloured solution.

sulphuric acid, in order to simplify the subsequent analysis. In the case of a complex ore or alloy, it is immaterial which acid is used, because it is usually necessary to precipitate the copper and arsenic groups together as sulphides, and afterwards to separate these by appropriate methods.

Electrolytic methods for the determination of bismuth have been proposed, but cannot be recommended.

A colorimetric method for the determination of traces of bismuth is described on p. 296.

Bismuth should be weighed as the oxide; the phosphate is a useful weighing form for large amounts of bismuth.

Forms in which Bismuth is precipitated

Basic Bismuth Carbonate.—This method is applicable in presence of sodium, potassium, and ammonium salts only. The results are inaccurate if the solution contains sulphate or chloride.

Metallic Bismuth.—This method is available in presence of zinc, aluminium, sodium, potassium, and ammonium salts.

Basic Bismuth Nitrate.—This method may be used to separate bismuth from all other metals except tin, antimony, and mercury.

Determination of Bismuth as Oxide after Precipitation as Basic Carbonate

OUTLINE OF METHOD.—The bismuth is precipitated by ammonium carbonate as basic bismuth carbonate, which is converted into oxide by ignition and weighed as Bi_2O_3 .

Basic Bismuth Carbonate is a granular, white precipitate, which is readily soluble in acids and slightly soluble in ammonia. If precipitated from a solution containing chloride or sulphate, it is always contaminated with basic chloride or sulphate. As these basic salts are not completely converted into oxide by ignition, the method is applicable only in absence of all salts other than nitrate.

Bismuth Oxide, Bi_2O_3 , is obtained when the basic nitrate or carbonate is ignited. Complete decomposition occurs on ignition at a low red heat. As the molten oxide attacks porcelain, it is inadvisable to heat above the temperature at which the oxide just melts. The oxide is readily reduced to metal by carbon, and the filter paper should therefore be completely incinerated before the precipitate is brought into the crucible.

Procedure.—Dilute the solution with water to about 50 ml. (a slight turbidity may be produced on dilution). Add ammonium carbonate in slight excess and boil until most of the ammonia is expelled. Filter, wash the precipitate with hot water, and dry. Incinerate the filter paper apart from the precipitate in a porcelain crucible, and oxidise any reduced oxide with nitric acid (compare p. 258). Transfer the main precipitate to the crucible and heat with a moderate flame—the heat being so regulated that the bismuth oxide is barely fused—and weigh as Bi_2O_3 .

Determination of Bismuth as Oxide after Precipitation as Metal

OUTLINE OF METHOD.—The bismuth is precipitated as metal by formaldehyde and alkali. The precipitated metal, which is usually contaminated with alkali, is dissolved in dilute nitric acid and reprecipitated as carbonate. By ignition, the carbonate is converted into the oxide, Bi_2O_3 .

Metallic Bismuth, as obtained by precipitation, is a black, spongy powder which is insoluble in water or in alkaline solutions.

Procedure.—To the bismuth solution, add about 10 ml. of 40 per cent. formaldehyde solution and excess of pure 10 per cent. sodium hydroxide solution. Warm on the steam-bath. When the precipitate has settled and the supernatant liquid has become clear, add a further 5 ml. of formaldehyde and a few millilitres of sodium hydroxide. Heat the solution until boiling, and press together with a glass rod the spongy precipitate of metal, in order to facilitate filtration. Filter, wash thoroughly with hot water, and then dissolve the precipitate with a little hot dilute nitric acid. Wash the filter paper several times with hot dilute nitric acid. Precipitate the bismuth as basic carbonate and convert to oxide, as described above.

Determination of Bismuth as Oxide after Precipitation as Basic Nitrate

OUTLINE OF METHOD.—The bismuth is obtained in solution as nitrate, and is precipitated as the basic nitrate by dilution and neutralisation. The basic nitrate is converted into oxide by ignition, and weighed as Bi_2O_3 .

Basic Bismuth Nitrate is usually a mixture of—



It is practically insoluble in cold water, and still less soluble in a very dilute solution of ammonium nitrate. It is readily soluble in acids that are not extremely dilute; in the precipitation, however, the solution should still contain a trace of acid, otherwise other metals are precipitated with the bismuth. If precipitated from a solution containing more than a trace of chloride, the precipitate is contaminated with bismuth oxychloride which is not completely converted into oxide by ignition.

Bismuth Oxide.—The properties of bismuth oxide are described on p. 323.

Procedure.—The bismuth solution must not contain more than a trace of chloride; if it contains chloride in quantity, add 5 ml. of concentrated nitric acid and evaporate to dryness or to a syrupy consistency; then add a further 5 ml. of nitric acid and again concentrate the solution. After this treatment the solution will be practically free from chloride.

To the bismuth nitrate solution, contained in a 700-1000 ml. beaker, add 500 ml. of water and 5 ml. of methyl orange solution. (Partial precipitation of the basic nitrate usually occurs on dilution.) Add ammonia drop by drop, with constant stirring, until the pink colour is almost discharged. Set the solution aside for one hour, and then filter. Wash with a dilute solution (2 grams per litre) of ammonium nitrate, dry at 100° , remove the precipitate as completely as possible from the paper, and incinerate the paper before addition of the precipitate (p. 245). The ignition of the precipitate should be carried out with the crucible covered, and with a very small flame at first, the temperature being raised slowly. If the heating is rapid, the gases given off during the decomposition of the nitrate carry away mechanically some of the solid. The final temperature should be barely sufficient to fuse the bismuth oxide.

BORATE

Boric acid or the borate in alkali borates, such as borax, may be determined by the volumetric method described on p. 98.

Mineral borates, such as borocalcite or boracite, or alkali borates containing carbonate, are first decomposed by boiling

with dilute hydrochloric acid under a reflux condenser. (The condenser is necessary in order to prevent loss of boric acid, which is volatile in steam.) The resulting solution is neutralised with sodium hydroxide using methyl orange as indicator, glycerol or mannitol is added, and the boric acid titrated as described on p. 98.

If appreciable quantities of iron and aluminium are present in the borate, this method of analysis leads to high results, and it is difficult to remove the iron and aluminium without at the same time losing some boric oxide. In order to obtain accurate results in such cases, and also in the analysis of silicates containing boric oxide, a distillation method, depending on the formation of volatile methyl borate, must be used. For a description of this method, see Mellor, *Quantitative Inorganic Analysis*, or Hillebrand, Lundell, Bright, and Hoffman, *Applied Inorganic Analysis*, 2nd Edition.

An ion exchange method has been put forward by Martin and Hayes (*Anal. Chem.*, 1952, **24**, 182).

The literature contains many colorimetric methods for boron, e.g. Ripley-Duggan, *Analyst*, 1953, **78**, 183; Naftel, *Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 407.

BROMIDE

Bromide is most readily determined volumetrically (see pp. 190 and 196).

Bromide may also be determined gravimetrically by precipitation as silver bromide. The procedure is identical with that adopted for the determination of chloride (see p. 255).

Silver Bromide is less soluble than the chloride. One litre of water dissolves 0.1 mg. at 20° and 3.7 mg. at 100°. It is insoluble in nitric acid, sparingly soluble in ammonia, and appreciably soluble in concentrated solutions of most salts. It is darkened, with partial decomposition, by light, though to a less extent than the chloride. It melts at 422° and acquires a darker colour. It can be dried completely at 105°.

CADMIUM

The separation of cadmium from certain metals, such as zinc, is a matter of some difficulty, and for methods of analysis

applicable to complex ores or alloys, reference should be made to larger text-books (see Appendix). The analysis of Wood's alloy (tin, lead, cadmium, and bismuth) is described on p. 422.

Cadmium may be determined polarographically (*e.g.* Hawkings and Thode, *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 71), colorimetrically (*e.g.* Wadelin and Mellon, *Anal. Chem.*, 1952, **24**, 894), or volumetrically (*e.g.* Walter and Freiser, *Anal. Chem.*, 1952, **24**, 1985).

Forms in which Cadmium is precipitated

Metallic Cadmium (Electrolytic).—This is a convenient and accurate method. For details, see p. 274.

Cadmium Sulphide.—This method serves to separate cadmium from metals of the iron, zinc, and calcium groups. If other members of the copper group are present, further treatment is necessary.

With 2-(*o*-Hydroxyphenyl)benzoxazole.—This method is highly selective for cadmium. Use of a tartrate buffer at *pH* 10.5 during the precipitation eliminates almost all interference. The interference of copper is eliminated by precipitating the copper first at a lower *pH*. Nickel and cobalt interfere if present in amounts greater than 20 mg., but can be removed before the cadmium is precipitated. See Walter and Freiser, *Anal. Chem.*, 1952, **24**, 984.

Determination of Cadmium as Sulphate after Precipitation as Sulphide

OUTLINE OF METHOD.—The solution is acidified with sulphuric acid, and the cadmium is precipitated with hydrogen sulphide. The cadmium sulphide is dissolved in hydrochloric acid, the solution evaporated to dryness with sulphuric acid, and the residue, CdSO_4 , is weighed.

Cadmium Sulphide is a yellow precipitate, insoluble in dilute acids or alkalis. It is readily soluble in concentrated hydrochloric acid. It may be completely precipitated by hydrogen sulphide from a solution that contains, in each 100 ml., 10 to 12 ml. of concentrated hydrochloric acid, or 5 to 7 ml. of concentrated sulphuric acid; under these conditions very little zinc will be precipitated with the cadmium. The precipitate is always contaminated with compounds such as $\text{Cd}_2\text{Cl}_2\text{S}$ or $\text{Cd}_2\text{SO}_4\text{S}$, and must therefore be converted into cadmium sulphate before it is weighed.

Cadmium Sulphate is colourless. It may be heated to a temperature approaching redness without decomposition. At a higher temperature it is slowly converted into oxide, becoming first yellow and then dark brown.

Procedure.—To the cadmium solution, add 5 ml. of concentrated sulphuric acid, dilute to 100 ml., and saturate with hydrogen sulphide. Filter, and wash with 5 per cent. ammonium nitrate solution. Dissolve the precipitate in the minimum amount of concentrated hydrochloric acid, wash the filter with hot dilute acid, and transfer the filtrate and washings to a large crucible. Add 0.5 ml. of concentrated sulphuric acid, and evaporate as far as possible on the steam-bath. Place the crucible inside a larger nickel crucible or an air-bath (Fig. 44, p. 237), and heat gently until no more fumes of sulphuric acid are given off. Weigh the CdSO_4 .

CALCIUM

Calcium may be determined volumetrically by the method given on p. 124 or by titration with EDTA (*e.g.* Banks, *Analyst*, 1952, 77, 484).

In gravimetric analysis, calcium is always determined by precipitation as oxalate, after removal of the copper, iron, and zinc groups. (For details, see pp. 262 and 439.)

CARBONATE AND BICARBONATE

Carbonate and bicarbonate may be determined volumetrically separately or together by means of standard hydrochloric acid (pp. 102; 103). Two gravimetric methods for either separately are in common use, viz. :—

1. A direct method, in which the carbon dioxide, expelled from the carbonate by the action of acid, is absorbed by soda-lime and weighed.

2. An indirect method in which the loss of weight from the escape of the carbon dioxide from an apparatus is ascertained.

Direct Method

OUTLINE OF METHOD.—A weighed quantity of the substance is mixed with dilute acid in a small flask connected with a series of drying tubes, and with two absorption tubes containing soda-lime. The soda-lime tubes are weighed before and after the experiment.

The Apparatus (Fig. 66) consists of the following :—

A. A distilling flask, of about 125 ml. capacity, provided with a rubber stopper and dropping-funnel. The stem of the latter should reach almost to the bottom of the flask, and the end should be drawn out to a point.

B. A **U**-tube, the open ends of which are sealed in the blowpipe flame, containing concentrated sulphuric acid. The acid is drawn in through one of the side-tubes, and the quantity is carefully adjusted until it is sufficient, *but no more than sufficient*, to seal the bend of the **U**-tube. The acid on the side-tube is volatilised by heating in a small flame.

C. A **U**-tube containing granulated pumice which has been soaked in concentrated copper sulphate solution, and

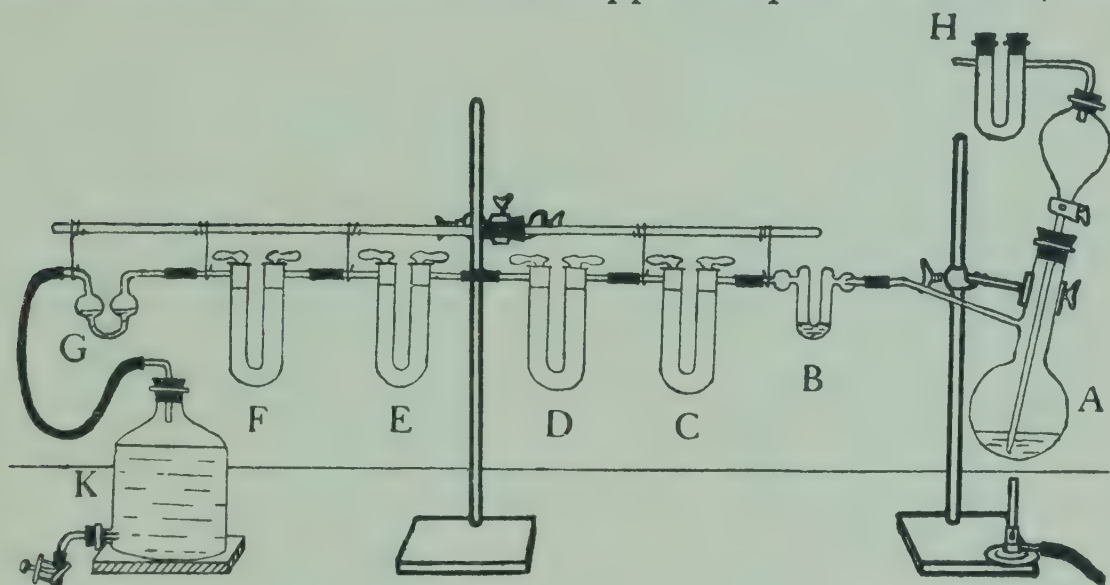


FIG. 66.

afterwards heated for several hours in an air-oven at 160° in order to partially dehydrate the copper sulphate. The object of this tube is to retain hydrogen sulphide arising from decomposable sulphides present in the substance, and any hydrochloric acid that may be carried over with the carbon dioxide.

D. A **U**-tube containing moderately fine granular calcium chloride, free from powder. The calcium chloride is introduced through a cylinder of glazed paper, and the tube is filled to within 2 cm. of the side-tubes. Loose wads of glass wool are then placed in each limb, any calcium chloride adhering to the upper part of the tube is removed, and the taps are made gas-tight with the minimum quantity of grease (Fig. 67).

In order to remove from the calcium chloride any free lime or basic chloride, which absorb carbon dioxide, a slow current

of dry carbon dioxide (p. 515) is passed through the tube for five minutes in order to displace the air; the outlet tap of the U-tube is then closed, and the tube is left attached to the Kipp generator for several hours or overnight. The carbon dioxide in the tube is then displaced by passing dry air through the tube for about fifteen minutes.

E. and F. Two U-tubes each containing soda-lime¹ and calcium chloride. A small wad of cotton-wool is placed near the middle of one limb, and fine granular soda-lime is introduced through a paper cylinder, so as to fill about three-fourths of the tube. The remaining fourth is filled with granular calcium chloride, and small wads of glass wool are placed in each limb (Fig. 68). The absorption of carbon dioxide by soda-

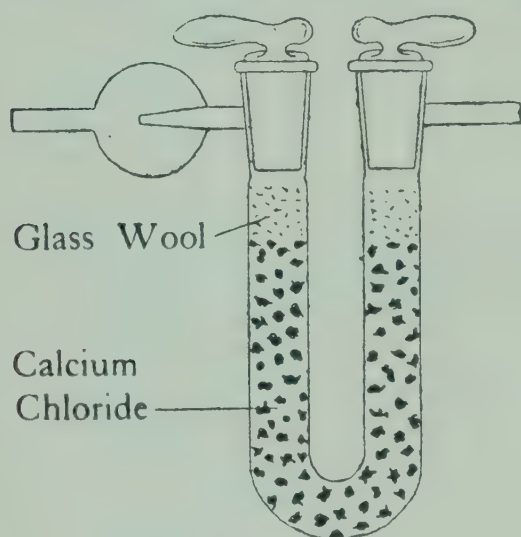


FIG. 67.

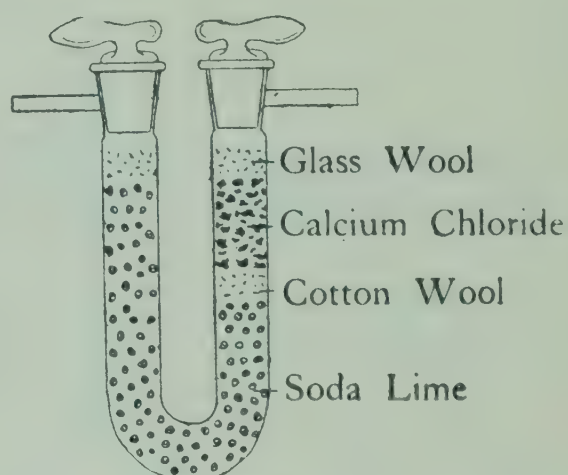


FIG. 68.

lime takes place with evolution of heat, and loss of the water which is formed at the same time is prevented by the calcium chloride.

G. A pulsimeter and guard-tube, containing a few drops of concentrated sulphuric acid. The latter protects the calcium chloride in the last U-tube from atmospheric moisture, and also shows the rate at which air leaves the apparatus.

H. A tube containing soda-lime which removes carbon dioxide from the air that is finally drawn through the apparatus.

K. An aspirator. An inverted wash-bottle without the jet and supported on a retort-stand ring may be used. The flow of water is regulated by means of a screw-clip.

¹ Soda-lime quickly deteriorates if exposed to the air, and soon becomes useless for the absorption of carbon dioxide. For this reason it is best to obtain it in *small*, well-sealed bottles.

The best form of **U**-tube is provided with hollow, ground-in glass taps. If plain **U**-tubes are used, they may be closed with tightly-fitting rubber stoppers, or with ordinary well-softened corks, which are cut off flush with the top of the tube and made gas-tight by brushing over with melted paraffin wax.

The contents of the **U**-tubes must be protected from atmospheric moisture and carbon dioxide. This is accomplished with the first form of **U**-tube by simply turning the taps; plain **U**-tubes must be provided with caps, fitted over the side-tubes, and made from short pieces of rubber tubing closed with pieces of glass rod. The **U**-tubes are supported by wire hooks attached to a glass rod held in a clamp. They are connected with each other by means of short pieces of thick-walled rubber tubing (pressure tubing) which are lubricated by rubbing the inner surface with a little graphite, any excess of which is carefully removed.

Procedure.—Carefully wipe the two soda-lime absorption tubes and leave them in the balance-room for fifteen minutes before weighing. (Remove the rubber caps before weighing.)

In general, the amount of substance taken for analysis should be so chosen that the increase in weight of the soda-lime tube is about 0.3 gram.

Weigh the carbonate (*e.g.* about 1 gram of calcspar or about 0.8 gram of sodium bicarbonate) in a small tube, about 2.5 cm. long and 1.3 cm. wide. Place the tube and contents in the distilling flask, and moisten with a few drops of water.

Set up the apparatus as shown in Fig. 66. The **U**-tubes are attached one after the other beginning with B, and the ends of the glass tubes should be brought close together inside each rubber junction. The absorption tubes E and F must be so placed that *the limbs containing calcium chloride are turned towards the aspirator*. The aspirator is not connected at this stage.

Test the apparatus as follows in order to find if it is gas-tight:—Attach a piece of glass tubing to the guard-tube G, and dip the tube into a beaker of water. Open all the taps, apply gentle suction at H in order to lift a column of water in the tube attached to G, and then close the tap of the dropping-funnel. The apparatus may be considered gas-tight if the level of the water in the tube remains constant for several minutes.

Now place about 20 ml. of dilute hydrochloric¹ acid in the dropping-funnel, open the tap carefully, and regulate the flow of acid and the evolution of gas, so that about two bubbles per second pass through the acid in B.

After a slight excess of acid has been added, and when the evolution of gas has become slow, close the tap of the dropping-funnel and (by means of a pipette) remove any acid remaining in the latter. Warm the contents of the flask very gradually with a small flame until the liquid just boils. Boil gently for about one minute, then lower the flame until boiling just ceases, *and open the tap of the dropping-funnel*. Attach the aspirator and the soda-lime tube H, and draw a slow current of air through the apparatus. As soon as the first soda-lime tube becomes cold, extinguish the flame, and continue the current of air for fifteen minutes more.

Detach the soda-lime tubes and, after wiping them, leave them in the balance-room for about half an hour before weighing. The weight of the tube F should remain practically constant, any increase amounting to not more than about 1 mg. A decided increase in weight shows either that the experiment was conducted too hurriedly, or that the soda-lime is unsatisfactory.

It is usual to calculate the percentage of carbonate in the substance as CO_2 .

Indirect Method

OUTLINE OF METHOD.—A weighed quantity of the substance is decomposed by dilute acid in an apparatus of special design, and the loss in weight of the apparatus, from the escape of carbon dioxide, is ascertained.

This method is not so accurate as the direct method (absorption by soda-lime), and its use is preferably restricted to the analysis of carbonates that can be decomposed by dilute *sulphuric* acid. If hydrochloric acid is used, its volatility makes it somewhat difficult to prevent loss of traces of that acid, and the result may be slightly high. In cases where an insoluble sulphate would be formed and sulphuric cannot be used, perchloric or phosphoric acid is preferable to hydrochloric acid as it is less volatile.

The Apparatus (Fig. 69) consists of a small, wide-mouthed

¹ In the absence of organic matter, perchloric acid may preferably be used instead of hydrochloric acid, as it is less volatile.

flask (100 to 120 ml.), of thin glass for the sake of lightness. The flask is fitted with a rubber stopper, through which pass a calcium chloride drying-tube and a tube that reaches nearly to the bottom of the flask and is drawn to a point at its lower end. The drying-tube is filled with granular calcium chloride with glass-wool plugs at either end, and the calcium chloride must be saturated with carbon dioxide, as previously described (see the direct method). If the carbonate is likely to contain sulphides or hydrochloric acid is to be used for the decomposition, one-third of the drying-tube B is filled with granular pumice which has been soaked in concentrated copper sulphate solution and dried at 160° , and two-thirds with calcium chloride. The acid required for the decomposition of the carbonate is

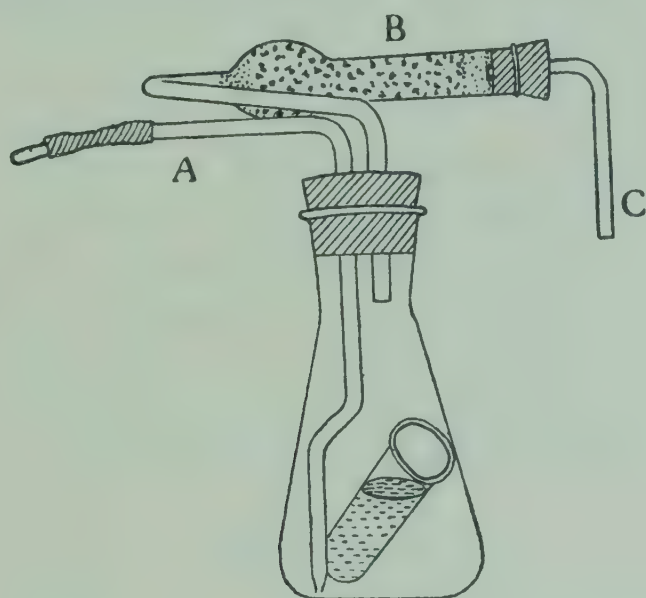


FIG. 69.

contained in a small test-tube, the length of which is so adjusted that the tube will stand obliquely in the flask, but cannot fall into a horizontal position. The tubes A and C are provided with rubber caps closed with short pieces of glass rod. Two additional straight calcium chloride tubes are also required.

Procedure.—Weigh the substance in the dry flask (*e.g.* about 2 grams of sodium carbonate crystals or about 1.5 gram of sodium bicarbonate). Measure a slight excess of dilute sulphuric acid (5 to 10 ml.) or of 20 per cent. perchloric acid (10 to 15 ml.) into the small test-tube, and fit the apparatus together. Allow it to remain in the balance-room for thirty minutes, remove the rubber caps, and weigh.

Replace the cap on the tube A, attach one of the supplementary calcium chloride tubes to C (in order to protect the

contents of B from atmospheric moisture) and, by carefully tilting the flask, allow the acid, a few drops at a time, to come into contact with the carbonate. The evolution of carbon dioxide must not be rapid, otherwise moisture may be carried away with the gas. When the whole of the acid has been mixed with the carbonate and effervescence has ceased, warm the flask cautiously with a *very small* flame until the liquid is heated almost to the boiling-point. Then attach an aspirator (K, Fig. 66) to C, and, the aspiration having been started, remove the cap on A, attach a calcium chloride tube to A, and draw a slow current of dry air through the apparatus for ten minutes. Remove the flame, continue the air current for ten minutes more, replace the caps on A and C, and after an interval of about thirty minutes, weigh the apparatus (without the caps).

The loss in weight represents the carbon dioxide expelled from the carbonate.

The Schrötter Apparatus.—This is a compact form made for this type of analysis. It consists of a decomposition flask with a side tubular and ground-glass stopper for the introduction of the carbonate. Above the flask is an acid reservoir fitted with a tap, and alongside a drying column containing concentrated sulphuric acid. The whole apparatus is light, and is used in a similar manner to that described on p. 333.

CHLORATE

Chlorate is usually determined by reduction to chloride (p. 196) and determination of the chloride by one or other of the methods mentioned below.

Volumetric methods for the determination of chlorate are described on pp. 149, 165, 177, and 196.

CHLORIDE

Chloride may be determined volumetrically by the methods given on pp. 190 and 195.

The gravimetric determination of chloride is described on p. 255.

For methods of separately determining chloride, bromide, and iodide in mixtures, reference may be made to Treadwell's *Analytical Chemistry*, vol. 2. The following method for the determination of chloride and bromide in a mixture is an example of an indirect method of analysis.

Chloride and Bromide in a Mixture by Indirect Analysis

OUTLINE OF METHOD.—A measured volume of the solution is treated with excess of silver nitrate, the precipitate is collected on a sintered glass crucible and weighed. Another equal volume of the solution is similarly treated, and the precipitate is filtered off on a sintered glass crucible, and washed, but not dried. The precipitate is then treated with concentrated ammonia, which dissolves it in the moist condition. The solution formed is treated with excess of potassium bromide solution and then acidified. The precipitate, which now consists of silver bromide only, is collected in the same sintered glass crucible, dried and weighed. This type of indirect determination, though of theoretical interest, gives results which are seriously affected by small experimental errors; great care must therefore be taken in carrying out the work.

Make up 100 ml. of a solution of pure sodium chloride and potassium bromide of accurately known concentration, approximately decinormal in each salt. Measure out 10 ml. of this solution and precipitate the halides with silver nitrate as described on p. 255, wash by decantation, and finally collect on a weighed No. 3 sintered glass crucible. Dry at 130° , and weigh the silver chloride and bromide precipitate. As it is very difficult to dissolve the dried precipitate in ammonia, it is discarded, and the adhering particles are removed with a concentrated solution of sodium thiosulphate, and the crucible washed, dried, and weighed again. Precipitate the halides in another 10 ml. of the original solution, wash by decantation, and filter off on the weighed crucible as before, and dissolve the moist precipitate in ammonia as follows: Wash out the filter flask, and drain it as thoroughly as possible. Replace the adapter carrying the crucible, and close the side tube of the flask with a piece of rubber tube and screw clip, after introducing a very slight excess pressure with the mouth. Add about 10 ml. of concentrated ammonia, and stir the precipitate with a short glass rod until it has practically all dissolved. It is not essential that it should dissolve completely, provided the same crucible is used for the final precipitate, since the silver chloride will pass into solution much more easily than the silver bromide. Attach the filter flask to the pump, draw the solution through the crucible, and wash the latter five times with 2 ml. portions of dilute ammonia. Transfer the contents of the filter flask to the beaker in which the mixed silver halides were precipitated, and wash the flask first with a little dilute ammonia, then with

water. To the solution in the beaker add 5 ml. of 10 per cent. potassium bromide, which will cause partial precipitation, then add dilute nitric acid until the solution is just acid. About 100 ml. of the acid will be required. Heat the solution to the boiling-point, allow it to cool, and after washing by decantation, collect the precipitate on the crucible in which the mixed silver halides were dissolved in ammonia. Wash the precipitate, dry at 130° , and weigh.

Let x and y respectively be the weights of NaCl and KBr in 10 ml. of solution, and w_1 and w_2 respectively the weights of AgCl+AgBr in the first precipitate, and the weight of AgBr in the second precipitate.

$$\frac{143.3}{58.45} x + \frac{187.8}{119.0} y = w_1$$

$$\frac{187.8}{58.45} x + \frac{187.8}{119.0} y = w_2$$

The values obtained for x and y should be compared with the weights of sodium chloride and potassium bromide used in making up the solution.

CHROMIUM

The volumetric method described on p. 148 is convenient and accurate.

When chromium is separated from other metals, it is first oxidised to chromate by fusion with sodium peroxide, or with a mixture of sodium carbonate and potassium nitrate; the chromate is determined volumetrically by the method already indicated, or gravimetrically as described below.

In the absence of all metals other than the alkalis, chromium may be determined by precipitation as hydroxide and conversion into oxide. The procedure is identical with that described under Aluminium on p. 254.

Chromic Hydroxide, when freshly precipitated, is a grey-green flocculent substance, insoluble in water. It is readily soluble in acids and in sodium hydroxide. It is sparingly soluble in ammonia, yielding a violet-red solution; if this solution is boiled, the ammonia is expelled and the chromic hydroxide is precipitated. When dried at 100° , it loses water

of hydration and becomes bluish-green. On ignition it is converted into chromic oxide, Cr_2O_3 .

Chromic Oxide is a dark green powder which may be ignited strongly without loss of weight. The oxide, after strong ignition, is insoluble in hydrochloric acid.

A colorimetric method is described on p. 297.

CHROMATE AND DICHROMATE

Chromate and dichromate are usually determined volumetrically (p. 148). If the methods are practicable, the gravimetric determination as mercurous chromate or as barium chromate is easy and accurate. Chromate (or dichromate) may also be determined gravimetrically by reduction to a chromic salt, followed by precipitation as chromic hydroxide (see under Chromium).

A colorimetric method is described on p. 297.

Forms in which Chromate is precipitated

Mercurous Chromate.—The presence of chloride or sulphate, except in small amount, renders this method inaccurate.

Barium Chromate.—Chloride does not interfere with the use of this method, but sulphate must, of course, be absent. The properties of barium chromate and its precipitation are described on p. 322.

Determination of Chromate as Chromic Oxide after Precipitation as Mercurous Chromate

OUTLINE OF METHOD.—The chromate is precipitated as mercurous chromate, which on ignition is decomposed, leaving chromic oxide, Cr_2O_3 .

Mercurous Chromate.—On addition of mercurous nitrate to a chromate, a brown precipitate of a basic salt separates. This quickly changes to the bright red, normal salt, Hg_2CrO_4 . Mercurous chromate is insoluble in water and in very dilute nitric acid. On ignition, it is converted into chromic oxide (for the properties of chromic oxide, see above). If the

mercurous chromate is contaminated with much mercurous chloride, the precipitate is bulky and inconvenient, and chromium is lost during the ignition.

Procedure.—Heat the neutral or slightly acid solution, and add mercurous nitrate until precipitation is complete. Keep the solution hot until the precipitate becomes bright red. Then add ammonia cautiously until a small quantity of a dark grey precipitate forms permanently. Heat until boiling, then cool, filter, and wash with a dilute mercurous nitrate solution. Dry the precipitate and the filter. Separate the precipitate and burn the filter before the addition of the precipitate. Ignite very gently at first and in a good draught, and finally ignite with the blowpipe. (**Caution.**—*The vapour given off during the ignition of the mercurous chromate is very poisonous.*) Cool, and weigh the Cr_2O_3 .

COBALT

Cobalt is determined after removal of those metals which are precipitated by hydrogen sulphide in acid solution. From the analytical point of view, cobalt shows an extremely close relationship to nickel and, with one exception, the methods indicated on p. 370 for the determination of nickel may be used without modification for cobalt. Cobalt (unlike nickel) is not precipitated by dimethylglyoxime, and one of the best methods of separating cobalt from nickel is based on this fact (see p. 371); another method of separation is described below.

A colorimetric method is described on p. 298.

Forms in which Cobalt is precipitated

Cobalt Sulphide.—Precipitation with ammonium sulphide serves to separate cobalt, nickel, manganese, etc., from the alkali and alkaline earth metals. Cobalt (and nickel) may be separated from manganese by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Cobaltic Hydroxide.—Cobaltic hydroxide is precipitated by bromine and sodium hydroxide, and the hydroxide is reduced to metallic cobalt.

Cobalt Salt of α -Nitroso- β -naphthol.—This compound of cobalt is insoluble in hydrochloric acid, whereas the corresponding nickel salt is soluble, and the method is very useful

for the separation of a small quantity of cobalt from a comparatively large quantity of nickel.

Cobalt Ammonium Phosphate.—The determination of cobalt by precipitation in this form and ignition to cobalt pyrophosphate is described by W. R. Schoeller (*Analyst*, 1944, 69, 8) as the most satisfactory method for cobalt present in substantial amounts. Other metals, the phosphates of which are insoluble in neutral or alkaline solution, must be absent.

Cobalt Oxinate.—By the use of this method cobalt may also be determined volumetrically.

Metallic Cobalt (Electrolytic).—The procedure is identical with that described for nickel on p. 273.

Determination of Cobalt by the α -Nitroso- β -naphthol Method

OUTLINE OF METHOD.—The cobalt is precipitated by means of α -nitroso- β -naphthol dissolved in acetic acid. The precipitate is washed, dried, and ignited. The cobalt oxide is either ignited in an atmosphere of hydrogen and the metallic cobalt weighed, or converted to sulphate.

α -Nitroso- β -naphthol, $C_{10}H_7O_2N$, when pure, is a yellow, crystalline substance, insoluble in water. The reagent is a freshly prepared solution obtained by stirring 1 gram of the solid in 60 ml. of glacial acetic acid for several minutes, then adding 40 ml. of water, and filtering. The cobaltic compound $(C_{10}H_6O_2N)_3Co$, is obtained as a voluminous brick-red precipitate which is insoluble in dilute hydrochloric acid. The nickelous compound, $(C_{10}H_6O_2N)_2Ni$, is soluble in hydrochloric acid.

Procedure.—Dilute the solution, containing not more than 0.05 gram of cobalt as sulphate or chloride, to 150 ml. and add 5 ml. of concentrated hydrochloric acid. Heat to about 70° and add 25 to 50 ml. (according to the amount of cobalt) of the hot reagent. Allow the precipitate to settle, and ascertain whether precipitation is complete by adding more reagent to the clear solution. Set aside for at least six hours. Filter through an 11-cm. paper. Wash the precipitate first with cold water, then with hot, dilute (4N) hydrochloric acid (in order to remove any nickel salt), and finally with hot water until free from acid. Dry the precipitate. Incinerate the paper together with the precipitate and about a decigram of pure

oxalic acid (in order to facilitate removal of carbon) in a Rose crucible if the cobalt is to be weighed as metal; raise the temperature very cautiously, and ignite finally with a Méker burner. Reduce the cobalt oxide (mainly Co_3O_4) by heating in a current of hydrogen. Cool, and weigh the metallic cobalt.

A more convenient though less accurate method is to incinerate the precipitate with oxalic acid in an ordinary crucible until all the carbon is burnt off. Add 2 ml. of 2N sulphuric acid, and evaporate as far as possible on the water-bath. Place the crucible inside a larger iron crucible, the bottom of which has been covered with a thin pad of asbestos. Heat the outer crucible gradually to dull redness. Then cool, and weigh the cobalt sulphate, CoSO_4 , which should not contain any black portions.

Determination of Cobalt as Phosphate

OUTLINE OF METHOD.—The cobalt solution is strongly acidified, ammonium phosphate solution added, and then ammonium hydroxide until the pH of the solution has reached a value between 8 and 9. The precipitate is either ignited to the pyrophosphate $\text{Co}_2\text{P}_2\text{O}_7$, or weighed on a Gooch or sintered glass crucible as cobalt ammonium phosphate $\text{CoNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$.

Cobalt Ammonium Phosphate at first separates in a blue flocculent form, which in the hot solution gradually becomes crystalline and lilac in colour, and in the latter form is easily filtered and washed. It is slightly soluble in excess of ammonium hydroxide and easily soluble in mineral acids.

Procedure.—Weigh accurately about 4 grams of cobalt ammonium sulphate or 3 grams of cobalt sulphate, dissolve it in water and make up the solution to 100 ml. Measure 25 ml. of the solution into a 350 ml. beaker, add 100 ml. of water, 10 ml. of concentrated hydrochloric acid, and about 1 gram of ammonium phosphate. Heat nearly to the boiling point, and while stirring add from a burette a solution of ammonium hydroxide made by diluting 20 ml. of the concentrated solution to 50 ml. with water. No permanent precipitate will be obtained until about 16 ml. of the ammonium hydroxide have been added. When a permanent precipitate has formed, add 2 ml. of bromo-thymol blue indicator, and run in the ammonium hydroxide in successive amounts of 0.5 ml., until, after the

precipitate has been stirred and allowed to settle, the supernatant liquid first shows a definite green colour. If bromothymol blue is not available, 2 ml. of phenolphthalein may be substituted, but in that case the supernatant liquid must finally have only a faint pink colour, otherwise the pH will be too high and must be reduced by adding a few drops of dilute hydrochloric acid and stirring. If the original blue precipitate has changed to the lilac form, it is not easy to detect the slight pink colour of the phenolphthalein without complete settling.

After the solution has stood for several hours, pour the supernatant liquid through an ashless filter and wash three times by decantation with 30 ml. lots of cold water. Test a little of the filtrate with ammonium sulphide, and in the unlikely event of a dark-coloured precipitate being formed, from cobalt in solution, add excess of ammonium sulphide, filter off and wash the precipitate on a separate filter. Ignite this and weigh as Co_3O_4 . Transfer the main precipitate to the first filter, and wash with cold water until free from sulphate. Ignite the precipitate with the paper in a porcelain crucible using a Bunsen burner, and weigh as $Co_2P_2O_7$.

Instead of being ignited to the pyrophosphate the cobalt ammonium phosphate may be collected on a Gooch or No. 3 sintered glass crucible, washed with cold water and finally with acetone, dried in the steam oven and weighed as the monohydrate $CoNH_4PO_4 \cdot H_2O$.

Determination of Cobalt as Oxinate

The use of oxine as a reagent is described under Aluminium (p. 316).

Procedure.—To the solution containing not more than 0.06 gram of cobalt add about 2 ml. of dilute hydrochloric acid and 25 ml. of 2N ammonium acetate. The final volume of the solution should be about 60 ml. Warm to about 60° , and run in from a burette 1 ml. of the oxine solution, prepared as described on p. 317, for every 3 mg. of cobalt present. After mixing, the solution should have a yellow colour showing the presence of excess of the reagent. Heat nearly to boiling, filter through a No. 3 sintered glass crucible, wash with hot water, dry at 150° , and weigh as $Co(C_9H_6ON)_2$.

Instead of the precipitate being dried and weighed, it may be

dissolved in warm 6N hydrochloric acid and aliquot parts titrated with a standard bromate-bromide mixture as described under Aluminium (p. 317). The volume of oxinate solution taken for titration should not contain more than 0.015 gram of cobalt. One ml. of decinormal bromate solution is equivalent to 0.737 mg. of cobalt.

COPPER

Copper may be determined volumetrically (pp. 159 and 184). In certain analyses copper is precipitated in acid solution, together with many other metals, by hydrogen sulphide.

A colorimetric method for the determination of traces of copper is described on p. 298.

Forms in which Copper is precipitated

Cupric Oxide.—This is a convenient and accurate method, but is seldom applicable, as other metals that give insoluble oxides may be present. For details, see p. 257.

Cuprous Thiocyanate.—Since most thiocyanates are soluble, this method is sometimes useful for the separation of copper from other metals. Lead, mercury, and silver interfere, their thiocyanates being also insoluble. The cuprous thiocyanate may either be weighed as described below, or estimated volumetrically (see p. 184).

Cupric Thiocyanate and Pyridine Complex.—This method obviates any necessity to reduce the copper to the cuprous state.

Metallic Copper (Electrolytic method).—This is probably the best method for separating copper from the other metals precipitated with it by hydrogen sulphide in acid solution. For details, see pp. 270 and 272.

Determination of Copper as Cuprous Thiocyanate

OUTLINE OF METHOD.—The copper is precipitated with ammonium thiocyanate in presence of sulphurous acid, and is weighed as cuprous thiocyanate.

Cuprous Thiocyanate, $\text{Cu}_2(\text{CNS})_2$, is a pure white, crystalline precipitate, almost insoluble in water and in dilute hydrochloric, sulphuric, and sulphurous acids. It may be dried without decomposition at temperatures not exceeding 150° .

The solution for analysis should be made *slightly* acid with sulphuric acid. Nitrates or other oxidising agents, if present, must be removed by evaporation with sulphuric acid.

Procedure.—Weigh out accurately about 0.5 gram of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, and dissolve it in about 100 ml. of water. Add 3 grams of sodium bisulphite, and 20 ml. of dilute sulphuric acid; or, preferably, add 5 ml. of dilute sulphuric acid, and excess of sulphurous acid. Then to the cold solution add ammonium thiocyanate solution drop by drop with constant stirring until all trace of blue colour has disappeared, carefully avoiding much excess. When the precipitate has settled (which may be after some hours), filter off on a Gooch crucible or sintered glass crucible, porosity 4, and wash with cold water until ferric chloride gives no coloration with the washings. Wash finally several times with 20 per cent. alcohol, dry at a temperature not exceeding 150° , and weigh as $\text{Cu}_2(\text{CNS})_2$. As an alternative, the precipitate may be estimated by titration with potassium iodate in the presence of a sufficient concentration of hydrochloric acid (see p. 184).

Determination of Copper as Cupric Thiocyanate and Pyridine Complex

Copper may be determined rapidly, in the absence of metals other than those of the alkali and alkaline earth groups and magnesium, by means of the complex formed between its thiocyanate and pyridine, $\text{Cu}(\text{CNS})_2 \cdot (\text{C}_5\text{H}_5\text{N})_2$. This compound is slightly soluble in pure water, and more soluble in acetone, but it is almost insoluble in absolute alcohol and ether. It is stable at temperatures below 60° .

Procedure.—Weigh out accurately between 0.3 and 0.4 gram of copper sulphate, and dissolve it in 100 ml. of water in a 250 ml. beaker. Add slowly from a pipette, while stirring, about 2 ml. of pyridine, and then 0.5 gram of ammonium thiocyanate, or 70 ml. of a decinormal solution of this salt. Allow the precipitate to settle, and decant the greater portion of the liquid through a weighed Gooch or sintered glass crucible (porosity 4). Transfer the precipitate with the remainder of the liquid to the crucible, and wash the beaker and precipitate with water containing 0.3 per cent. of pyridine and ammonium thiocyanate, or, preferably, with water which has been

saturated with precipitate by shaking it with a portion of precipitate previously prepared. Complete the washing with two or three portions of absolute alcohol, followed by ether, each containing a trace of pyridine. Acetone must not be used. Dry in a vacuum until the weight is constant. The drying can be accelerated by previously warming for a short time in an air-oven at a temperature not exceeding 45°.

CYANIDE

A volumetric method for the determination of cyanide is described on p. 191.

DIOXIDE

Dioxides such as manganese dioxide and lead dioxide may be determined volumetrically as described on pp. 120, 121, 165, 166 and 184.

DITHIONITE (HYPOSULPHITE)

OUTLINE OF METHOD.—A weighed amount of sodium dithionite is added to an excess of silver oxide dissolved in ammonia (thus avoiding air oxidation) whereby an equivalent quantity of the silver complex is reduced. The silver deposited is collected, washed, dried, and weighed in a sintered glass crucible. Alternatively the silver may be dissolved in nitric acid and the silver nitrate titrated with standard thiocyanate.

Sodium dithionite is a strong reducing agent, and it should be exposed as little as possible to atmospheric oxygen. It reacts with silver oxide dissolved in ammonia according to the following equation :—



Procedure.—Add dilute ammonia to about 70 ml. of approximately decinormal silver nitrate in a beaker, until the precipitate of silver oxide first formed is redissolved, and then add an excess of about 5 ml. of ammonia. Place about 1 gram of sodium dithionite in a stoppered weighing bottle and weigh it accurately. Transfer about 0.3 gram directly into the beaker containing the ammoniacal silver solution while stirring continuously. Reweigh the weighing bottle, to determine the amount of solid transferred. Pour the supernatant liquid through a weighed No. 3 sintered glass filter, using only gentle

suction to avoid drawing through any of the finely divided silver which remains suspended in the solution. Wash by decantation three or four times with distilled water, and transfer the silver to the filter and wash it until a little of the filtrate collected separately gives no precipitate with hydrochloric acid. Dry the crucible at 130° , and weigh.

Instead of the silver being weighed it may be dissolved in nitric acid and titrated with standard thiocyanate solution. This can be done by washing out the filter flask, adding a hot mixture of 5 ml. of concentrated nitric acid and 5 ml. of water to the crucible and covering it with a watch-glass. When the action of the acid has ceased, draw the solution through into the flask (avoiding any contact with rubber). Repeat the treatment with hot acid and water, and finally wash the crucible and watch-glass thoroughly with distilled water. Transfer the filtrate to the beaker in which the silver was precipitated, boil to remove oxides of nitrogen, and cool. Titrate the silver nitrate with standard thiocyanate solution as described on p. 194.

FERRICYANIDE—FERROCYANIDE

Volumetric methods for the determination of these compounds are given on p. 173 (ferricyanide), and pp. 150 and 153 (ferrocyanide). An electrometric method for ferrocyanide is given on p. 219.

FLUORIDE

Gravimetric, colorimetric, and volumetric methods are used for the determination of fluoride. Gravimetrically, fluoride is usually precipitated and weighed as calcium fluoride. One of the simplest methods of determining fluorine in fluorides, or in silicates decomposable by sulphuric acid, is to expel the fluorine as silicon fluoride and measure the volume of the gas. A full description of various methods of determination is given in Mellor's *Quantitative Inorganic Analysis*, and in Hillebrand, Lundell, Bright, and Hoffman's *Applied Inorganic Analysis*, 2nd Edition.

A volumetric method for the determination of fluoride is given on p. 203.

Determination of Fluoride in a Silicate Rock

OUTLINE OF METHOD.—The powdered substance is fused with sodium carbonate and the resulting mass extracted with water and filtered. After removal of the silica and bases from the solution by means of ammonium carbonate, calcium chloride is added, and the precipitated calcium fluoride and calcium carbonate is ignited. The calcium carbonate is removed with acetic acid, and the residual calcium fluoride is ignited and weighed.

Calcium Fluoride is a white, gelatinous precipitate, sparingly soluble in hydrochloric and nitric acids, and nearly insoluble in acetic acid. It is more soluble in presence of ammonium salts. The precipitate is very difficult to filter off, but if it is precipitated together with some calcium carbonate it is much easier to filter off. Calcium fluoride cannot be completely decomposed by fusion with sodium carbonate unless it is mixed with silica or a silicate.

Procedure.—Weigh accurately in a platinum crucible about 2 grams of the rock powder and mix it with 12 grams of dry sodium carbonate. (In the case of a fluoride containing but little silica, 4 grams of silicic acid must also be added.) Heat the mixture gradually to redness, and maintain the temperature until effervescence ceases (*cf.* p. 386). Do not use the blowpipe. After cooling, place the crucible in a large porcelain basin or casserole, and extract the mass thoroughly with hot water, taking care to break down any large lumps. Filter, and wash with hot water. The filtrate contains all the fluoride.

Add about 10 grams of ammonium carbonate and set aside for about twelve hours in a warm place. Filter off the precipitated silica and alumina, and wash with dilute ammonium carbonate solution. Heat the covered beaker containing the filtrate on the steam-bath until the ammonium carbonate is decomposed and the evolution of carbon dioxide ceases. In order to remove the last traces of silica, add about 5 ml. of a solution of precipitated zinc oxide in 10 per cent. ammonia, and evaporate until the smell of ammonia disappears. Filter, and wash with water.

Add dilute nitric acid to the filtrate until the alkali carbonate is nearly, but not entirely, decomposed. If too much acid is added, make the solution alkaline again with sodium carbonate. Then add excess of calcium chloride, and heat until boiling. Filter off the precipitated calcium fluoride and calcium carbonate on ashless paper pulp, wash with hot water, dry, and ignite

at a low red heat in a platinum crucible. Cool and add sufficient acetic acid to dissolve the calcium carbonate and oxide; warm the covered crucible on the steam-bath until effervescence ceases, and then evaporate to dryness. Extract with hot water containing a few drops of acetic acid, filter, wash, and ignite the residue. Repeat the extraction with very dilute acetic acid, and finally ignite to faint redness and weigh the CaF_2 .

It is advisable to check the result by converting the calcium fluoride into calcium sulphate. Add a few drops of concentrated sulphuric acid and evaporate carefully in a fume cupboard (Fig. 13, p. 37, or Fig. 44, p. 237). Ignite at a low red heat, and weigh the CaSO_4 .

GOLD

OUTLINE OF METHOD.—Gold is determined by reduction of its compounds by means of hydroquinone, the resulting metal being weighed.

Ferrous sulphate, sulphur dioxide, and oxalic acid are often used as reducing agents, but hydroquinone has advantages over these. The use of ferrous sulphate involves the subsequent separation of iron from the platinum metals if these are present; sulphur dioxide tends to bring down platinum together with the gold; and oxalic acid is slow in reduction, and the fine state of division of the gold makes filtration difficult.

Precipitation is carried out in hydrochloric acid of rather more than normal concentration, under which conditions the platinum metals, even if present in amounts double that of the gold, are not precipitated. The gold is also separated from such common metals as copper, zinc, and nickel, though the action of the reducing agent should not be prolonged beyond the period indicated in any determination. Tungsten interferes and must be removed if present.

Procedure.—If aqua regia has been used to dissolve the metal, evaporate the resulting solution three times with small amounts of concentrated hydrochloric acid, after the addition of a little sodium chloride, to remove excess of nitric acid. Dissolve the residue in 15 ml. of water, and 8 ml. of concentrated hydrochloric acid. Filter the solution through a small filter, wash, and dilute the solution to about 50 ml. The amount of gold present should be not more than 0.1 gram.

If the gold to be determined is already present in solution

as chloride, a volume containing not more than 0.1 gram of gold is taken, 8 ml. of concentrated hydrochloric acid are added, and the mixture adjusted to about 50 ml.

Heat the prepared solution, and add a freshly prepared 1 per cent. aqueous solution of hydroquinone from a dropping-funnel (p. 261), using 30 ml. of the reagent, while stirring continuously. Boil the mixture gently for fifteen minutes, and filter through a small paper filter, neglecting any brown colour in the filtrate. Wash repeatedly with hot water, dry, ignite in a *porcelain* crucible, and weigh.

HYDRAZINE—HYDROXYLAMINE

Volumetric methods for the determination of these compounds are described on pp. 181 and 182.

HYPOCHLORITE

The only common hypochlorites are those of calcium and sodium. Volumetric methods are described on pp. 167 and 175, and a gas-volumetric method on p. 491.

HYPOSULPHITE (*see* DITHIONITE)

IODIDE

Iodide is readily determined by the volumetric methods described on pp. 153, 183, 190 and 195.

It may also be determined gravimetrically by precipitation as silver iodide. The procedure is identical with that given for the determination of chloride (p. 255), except that there is no need to protect the precipitate from light.

Silver iodide is much less soluble in almost all solvents than either the chloride or bromide. The solubility in water is negligibly small (0.003 mg. per litre at 20°). It is practically insoluble in dilute nitric acid and very sparingly soluble in ammonia (35 mg. per litre in 10 per cent. ammonia at 15°). It is appreciably soluble in concentrated silver nitrate and other salt solutions. Silver iodide fuses, without decomposition, at 552°.

IRON

On account of its rapidity and accuracy, a volumetric determination of iron (see Index) is preferable to any gravimetric method.

A volumetric method may often be applied after the iron has been separated by precipitation from most other metals, and it is one of the best methods for the determination of the iron in a mixed precipitate of ferric and aluminium oxides (compare pp. 438 and 443).

In gravimetric analysis, iron is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. It is sometimes precipitated, together with aluminium, chromium, titanium, manganese, nickel, cobalt, and zinc, by ammonium sulphide, and is then separated from the other metals. In absence of the other metals of this group, it is preferable to precipitate iron and aluminium as hydroxides with ammonia.

The separation of iron from manganese, etc., is a matter of some difficulty. The "cupferron" method, described below, is easier, more rapid, and no less accurate than the older basic acetate method. Iron and manganese can also be separated satisfactorily in one operation by ammonium hydroxide under carefully controlled conditions (p. 351). For a similar separation of iron and zinc, see p. 352.

Colorimetric methods for the determination of traces of iron are described on pp. 290, 292, and 293.

Forms in which Iron is precipitated

If not already in the ferric state, the iron is always oxidised before precipitation as hydroxide, ferrous hydroxide being slightly soluble.

Ferric Hydroxide.—This is the easiest gravimetric method for the determination of iron, but is of limited applicability. For details of the precipitation where other metals which might interfere are absent, see p. 251.

Basic Ferric Acetate.—This method provides a separation from manganese, zinc, nickel, and cobalt, but aluminium is precipitated with the iron. For details, see under Aluminium, p. 314.

Ferric Salt of Nitrosophenyl Hydroxylamine ("Cupferron" Method).—Iron is precipitated by "cupferron" from

strongly acid solutions. This method provides a complete separation of iron from many metals and is particularly useful for the separation of iron from aluminium, manganese, and chromium. For details of metals precipitated see Furman, Mason, and Pekola, *Anal. Chem.*, 1949, **21**, 1325.

Determination of Iron by the "Cupferron" Method

OUTLINE OF METHOD.—The iron (in the ferric state) is precipitated from a strongly acid solution by "cupferron," and the precipitate is converted into ferric oxide by ignition.

Cupferron is the ammonium salt of nitrosophenyl hydroxylamine, $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$. It precipitates most of the heavy metals from neutral solutions as insoluble salts but not from acid solutions. The method is therefore useful for the separation of iron from manganese, aluminium, etc. The separation is remarkably complete, but in cases where large amounts of aluminium, manganese, or chromium are present, a second precipitation is advisable.

The precipitate of the ferric salt is rather bulky, and the amount of material taken should therefore be such as to yield about 0.1 gram of ferric oxide. The solubility of the precipitate appears to be negligible, even in 4N hydrochloric acid.

Procedure.—To the solution add 20 ml. of concentrated hydrochloric acid and dilute to 100 ml. Dissolve about 3 grams of cupferron in 50 ml. of cold water, and add it slowly and with constant stirring to the ferric salt solution. A brownish-red precipitate, which is partly crystalline and partly amorphous, separates. Excess of cupferron is shown by the formation of a white precipitate in the supernatant liquid. Stir well, but do not heat the solution.

Filter with suction. If the precipitate adheres tenaciously to the beaker, dissolve it in a little ether and then remove the ether by addition of a little boiling water.

Wash with cold water until almost free from acid, then twice with 6N ammonia to dissolve copper if this should be present, and finally twice with water. Place the wet paper and precipitate in a porcelain crucible and heat gently until no more inflammable gases are given off. Ignite, and weigh the ferric oxide obtained.

Exercise.—Determine the percentage of iron in ferric alum.

Separation of Iron from Manganese by Ammonium Hydroxide.

These metals can be separated almost completely in one operation by precipitation of the iron in the ferric state by ammonium hydroxide in presence of ammonium chloride if the final pH of the solution is carefully controlled. Ferric hydroxide is precipitated at a much lower pH than manganese hydroxide, the approximate figures being pH 4 and pH 9 respectively. Methyl orange changes colour over the range pH 3.1 and pH 4.4, so that if ammonium hydroxide is added to a mixed solution of ferric and manganese ions, containing methyl orange and ammonium chloride, until the colour of the indicator has just changed from orange to yellow, the iron will be almost completely precipitated, while only traces of manganese are carried down, even if filtration of the ferric hydroxide is delayed for several days. It is not easy to see the colour change of methyl orange in presence of ferric hydroxide, and therefore the approximate amount of ammonium hydroxide required should be found by a preliminary test, and the directions below should be followed closely. The separation is improved by precipitating the ferric hydroxide in a small volume of solution, as this results in a more compact form of precipitate which shows less tendency to occlude other cations, and is easier to wash by decantation than the bulky precipitate usually obtained.

Prepare a mixture of iron and manganese for the separation by weighing accurately about 8.5 grams of ferric alum and 3.5 grams of manganese chloride ($MnCl_2 \cdot 4H_2O$), dissolving these in water containing 5 ml. of dilute sulphuric acid, and making up to 100 ml. in a graduated flask. Approximately normal ammonium hydroxide (preferably freshly prepared by dissolution of ammonia) will be required.

To determine the approximate amount of ammonium hydroxide for neutralising the free acid and precipitating the iron, measure out 10 ml. of the mixture into a small beaker, add about 40 ml. of water and 5 ml. of methyl orange, and while stirring run in the normal ammonium hydroxide slowly until a permanent precipitate appears. If after this has settled for two minutes the upper clear layer has an orange or pink tint on looking through it, add successive portions of 0.5 ml. of N ammonium hydroxide until, after stirring and allowing

to settle each time, the supernatant layer is yellow. Note the volume added, which in this mixture of iron and manganese should be a little over 6 ml. Discard this test solution, and measure two more 10 ml. lots of the iron and manganese mixture into small beakers (preferably 100 ml.) for duplicate analyses. To each add 5 grams of ammonium chloride and treat both as follows. Run in the normal ammonium hydroxide at a rate of about one drop per second, while stirring vigorously to prevent a local concentration of ammonia, up to 0.5 ml. short of the amount required in the preliminary test. Dilute with 50 ml. of water, mix thoroughly, and allow to settle for a minute. If the liquid at the top is still brown and the precipitate does not settle easily, add another 3 drops of ammonium hydroxide while stirring, and allow to settle. Repeat if necessary until the precipitate settles quickly, leaving a practically colourless liquid above. Then add 2 ml. of methyl orange, stir and allow to settle. If the supernatant liquid is pink, stir and add 2 more drops of ammonium hydroxide. Repeat if necessary until 2 drops change the colour of the supernatant liquid from faintly pink to yellow. Allow to settle completely and pour the clear liquid through an ashless filter. Wash three times by decantation with 4 per cent. ammonium nitrate, adding about 60 ml. each time. Transfer the precipitate to the filter and wash with 4 per cent. ammonium nitrate until no reaction is obtained for sulphate in a few millilitres of the filtrate. Ignite the precipitate at a high temperature and weigh as Fe_2O_3 . Evaporate the combined filtrates to about 150 ml. and precipitate the manganese as manganese carbonate with ammonium carbonate as described on p. 363. It is not necessary to add more ammonium salts.

Aluminium cannot be separated satisfactorily from manganese by this method because, in order to precipitate all the aluminium, it would be necessary to raise the pH of the solution to a higher value than is required in the case of iron, and this would result in the partial precipitation of manganese, especially on standing.

Separation of Iron from Zinc by Ammonium Hydroxide.

The separation of these metals can be carried out by means of ammonium hydroxide in presence of a high concentration of ammonium chloride. Precipitation of ferric hydroxide is

made in a very small volume and the precipitate must be washed with a solution containing ammonium hydroxide as well as an ammonium salt. The compact form of ferric hydroxide obtained under these conditions has less tendency to occlude other cations, and is more easily filtered and washed than that produced in the ordinary way.

Weigh out accurately about 8 grams of ferric alum and 4 grams of zinc sulphate. Dissolve these in water containing about 5 ml. of dilute sulphuric acid, and make up to 100 ml. in a graduated flask. Measure out 25 ml. into a small beaker (100 ml.), add about 10 drops of concentrated hydrochloric acid and evaporate on a hot plate to about 3 ml., taking care that the bottom of the beaker does not become dry at any place towards the end of the evaporation. This can be avoided by holding the beaker and giving it a swirling motion over a small flame when most of the liquid has been evaporated. Now add 5 grams of ammonium chloride and, while mixing with a rod, run in slowly 10 ml. of approximately 12N ammonium hydroxide (prepared by diluting 32 ml. of 0.880 sp. gr. ammonium hydroxide to 50 ml.). Dilute with about 60 ml. of water, stir and allow to settle. Pour the supernatant liquid through an ashless filter, and wash four times by decantation with a solution containing 5 grams of ammonium chloride and 5 ml. of 12N ammonium hydroxide in 100 ml. Transfer the precipitate to the filter and wash with this solution until free from sulphate. Then wash the ferric hydroxide twice with 1 per cent. ammonium nitrate to remove most of the chloride, but discard these washings.

Ignite and weigh the precipitate as ferric oxide as described on p. 254. The zinc in the filtrate may be determined gravimetrically as zinc ammonium phosphate (p. 406), or volumetrically with potassium ferrocyanide (p. 199).

The separation of aluminium from zinc by this method is less satisfactory, because a small amount of aluminium would remain in solution in presence of the considerable excess of ammonium hydroxide required to prevent precipitation of the zinc.

LEAD

In the analysis of a mixture, lead is usually determined as sulphate, although the chromate method is preferable if it can

be used. The separation of lead from calcium by precipitation as sulphide is described in connection with the analysis of glass (p. 450).

A volumetric method for the determination of lead is described on pp. 100 and 125.

A colorimetric method is described on p. 299.

Forms in which Lead is precipitated

Lead Sulphate.—This method provides a separation from all metals except barium, strontium, calcium, and mercury.

Lead Chromate.—This method is more accurate than the sulphate method, but is limited in applicability on account of the general insolubility of chromates.

Lead Dioxide (Electrolytic).—Lead may be separated from almost all other metals by this method. For details, see p. 276.

Determination of Lead as Sulphate

OUTLINE OF METHOD.—The solution is evaporated with concentrated sulphuric acid until all hydrochloric or nitric acid is expelled. After dilution, the lead sulphate is filtered off, washed with alcohol, dried, and weighed as PbSO_4 .

Lead Sulphate is a heavy, white powder which is sparingly soluble in water. One litre of water at 18° dissolves about 40 mg. of the salt. It is much less soluble in dilute sulphuric acid, but with increasing concentration of sulphuric acid the solubility again increases. It is readily soluble in hot concentrated hydrochloric and nitric acids. It is soluble in solutions of almost all ammonium salts and in solutions of alkali hydroxides, but is almost insoluble in alcohol. It may be heated to a bright red heat without decomposition if reducing gases are excluded from the crucible. At a red heat, it is readily reduced by carbonaceous matter, with loss of lead by volatilisation.

Procedure.—To the lead solution add 3 ml. of concentrated sulphuric acid, and evaporate in a porcelain basin on the steam-bath and then over a Rose burner until dense white fumes are evolved. Cool, dilute to about 100 ml. with cold water, and stir. The precipitate may be filtered off more readily if it is kept for a few hours before filtration. Filter off on a Gooch or sintered porcelain crucible (porosity 4). Wash the

precipitate several times with the minimum quantity of N sulphuric acid, and finally with alcohol. Dry at 100° , place the crucible inside a nickel crucible, and heat to constant weight.

Determination of Lead as Chromate

OUTLINE OF METHOD.—The lead is precipitated as chromate by the addition of potassium chromate or dichromate. The precipitate is collected in a Gooch or sintered glass crucible, dried at 120° , and weighed as PbCrO_4 .

Lead Chromate is almost insoluble in water and in acetic acid (1 litre of water dissolves 0.1 mg. at 18°), slightly soluble in nitric acid, and readily soluble in alkali solutions. It may be dried completely at 120° , but loses oxygen if heated to its melting-point.

Procedure.—If the solution is neutral or alkaline, add acetic acid until it is distinctly acid. If the solution contains nitric acid, add sufficient sodium acetate (5 to 10 grams) to replace the nitric acid by acetic acid. To the hot solution add potassium dichromate (2 per cent. solution) in slight excess. Place the beaker on the steam-bath until the precipitate settles. Examine the supernatant liquid, which must be coloured slightly orange. Filter off on a Gooch or sintered glass crucible (porosity 4), wash thoroughly with hot water, and dry at 120° .

LITHIUM (POTASSIUM AND SODIUM)

Lithium, potassium, and sodium often occur together, and if the material to be analysed contains the three metals, they are first separated from all other metals. They are then converted into chlorides, completely dehydrated, and ammonium salts (if present) driven off by volatilisation. Lithium chloride is extracted by means of a suitable organic solvent, leaving the sodium and potassium chlorides undissolved. The lithium in the extract is finally weighed as sulphate.

Whilst the potassium and sodium in the residue may be determined by a direct method, as described under these metals, the amount of each present may also be found by weighing the two chlorides together, and determining either one of the metals or the total chloride present, and calculating the weights of the two metals from the data obtained.

The preliminary extraction of lithium, sodium, and potassium in an insoluble silicate is described on p. 445.

Lithium may be determined by flame photometry (see p.510).

Treatment of the Solution for Analysis

If metals other than the alkali metals and acid radicals other than chlorides are present, the following treatment must be carried out. Evaporate the solution with a slight excess of sulphuric acid, and heat carefully until thick white fumes are evolved. Cool, dilute, and to the hot solution add a slight excess of barium chloride solution. Boil for a few minutes, cool slightly, and without filtering make the solution alkaline with ammonium hydroxide. Add ammonium carbonate solution in sufficient amount to precipitate the excess of barium and other metallic radicals. Boil, wash by decantation, and filter. Wash the residue until all chlorides are extracted. Evaporate the filtrate to dryness, and gently ignite to remove ammonium salts, avoiding fusion in the process, and observing the precautions described on p. 384, under the determination of sodium and potassium. Dissolve the residue, and precipitate traces of barium (and calcium) still present by the addition of a few drops of ammonium hydroxide, ammonium carbonate, and ammonium oxalate. Filter through a small filter, wash, evaporate the filtrate, and again gently ignite.

The lithium chloride must now be separated from the potassium and sodium chlorides in the following manner.

Determination of Lithium in the presence of Sodium and Potassium

OUTLINE OF METHOD.—All metals other than lithium, sodium, and potassium, and all acid radicals other than chloride having been removed as described above, the completely anhydrous solid is extracted with anhydrous acetone, which dissolves the lithium chloride alone. *Lithium chloride* is soluble in many organic liquids in which the chlorides of the other alkali metals are inappreciably soluble. Such solvents include amyl alcohol, isobutyl alcohol, acetone, and dioxan. Of these acetone is the most convenient. Dioxan (recently suggested) is liable to peroxidation and may give rise to dangerous explosions on distillation. Lithium chloride fuses at 606°, and volatilises at this temperature.

Procedure.—Dissolve the solid containing only the chlorides of lithium, sodium, and potassium in the least possible amount

of water in a porcelain crucible (or small dish) which has been previously weighed with a watch-glass cover. Add 5 to 10 drops of concentrated hydrochloric acid and evaporate as far as possible on a water-bath, cover the crucible with the watch-glass, and heat in an air-oven at 160° for an hour.

In the meanwhile, support a No. 3 sintered glass crucible just below the top of a wide-mouthed 250 ml. flask or bottle, using either platinum wire or thread which has been previously extracted with acetone. The wire or thread may be conveniently held in position by a rubber band round the outside of the flask. Bore a cork to carry a small reflux condenser and extract the cork with acetone to remove soluble matter.

After cooling in a desiccator the crucible containing the chlorides, rapidly weigh it covered with the watch-glass, and immediately after weighing transfer as much as possible of the solid to the sintered glass crucible in the extraction flask. This can be done with the aid of a short piece (5 cm.) of glass rod flattened at the end, and a jet of anhydrous acetone from a small wash-bottle. The glass rod is then left inside the sintered glass crucible, and the reflux condenser is attached to the flask without delay, in order to avoid absorption of moisture. Add more anhydrous acetone through the condenser until about 50 ml. are present. Heat on the water-bath for three hours, regulating the flame so that the solid in the crucible is covered throughout by the condensed acetone. Meanwhile gently ignite the crucible from which most of the mixed chlorides were transferred, cool and weigh it with the watch-glass. From the loss in weight the proportion of the original mixed chlorides transferred may be calculated and an allowance made for the small amount which remains behind.

After the extraction is finished, cool and remove the crucible containing the residue of sodium and potassium chlorides, which may be determined if desired as described on p. 384. Distil off the acetone in the flask, and determine the lithium either by titrating a suitable portion with standard silver nitrate, or by converting it to lithium sulphate as described below.

Determination of Lithium as Lithium Sulphate

OUTLINE OF METHOD.—A slight excess of sulphuric acid is added to the lithium salt solution in a small dish. The mixture is evaporated to dryness, and ignited to lithium sulphate, Li_2SO_4 . Other metals, and acid radicals not converted to sulphate by this treatment, must be absent.

Lithium Sulphate is more easily obtained free from the bisulphate by ignition than are the other alkali metal sulphates. It is therefore unnecessary to add ammonium carbonate for the final ignition. The sulphate is not volatile at a dull red heat.

Procedure.—Weigh out accurately about 0.3 gram of lithium chloride in a stoppered weighing bottle, the salt being very hygroscopic. Transfer the contents to a small weighed dish, preferably of platinum, using as little water as possible. Add 0.5 ml. of concentrated sulphuric acid to the solution, and evaporate to dryness on the water-bath. Heat with a very small flame until no further evolution of white fumes is noticed; then raise the temperature to a dull red heat, maintain this for about fifteen minutes, cool, and weigh. Repeat the ignition until the weight is constant.

MAGNESIUM

Magnesium can be determined volumetrically after precipitation as oxinate (p. 361), or by titration with EDTA (p. 206, or see *e.g.* Banks, *Analyst*, 1952, **77**, 484).

Traces of the metal may be determined colorimetrically, *e.g.* Harvey, Komarmy, and Wyatt, *Anal. Chem.*, 1953, **25**, 498; Drosdorff and Nearpass, *Anal. Chem.*, 1948, **20**, 673.

Forms in which Magnesium is precipitated

Magnesium Ammonium Phosphate.—This is the method in common use. The process takes considerable time, and to obtain correct results the conditions of procedure laid down must be carefully observed.

In the analysis of a mixture by this method, metals belonging to the copper, iron, zinc, and calcium groups must first be removed. A typical example of the separation of magnesium from calcium and other metals is described on pp. 438 to 441.

Magnesium Oxinate.—Other metals precipitated by oxine must first be removed.

Determination of Magnesium as Pyrophosphate after Precipitation as Magnesium Ammonium Phosphate

OUTLINE OF METHOD.—The magnesium is precipitated as magnesium ammonium phosphate by means of ammonium hydrogen phosphate and ammonia. The precipitate is either converted into magnesium pyrophosphate by ignition, and weighed as $\text{Mg}_2\text{P}_2\text{O}_7$, or it may be weighed directly as the hexahydrate of magnesium ammonium phosphate.

Magnesium Ammonium Phosphate, $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, is a white, crystalline substance which is somewhat soluble in water. At the ordinary temperature, 1 litre of water dissolves about 65 mg. It is much less soluble in ammonia.

In order to obtain a precipitate of normal composition (MgNH_4PO_4), the solution must be just acid until after the phosphate solution has been added, and the ammonia must be added last. If the precipitation takes place in the presence of much ammonium salt, the precipitate contains $\text{Mg}_3(\text{PO}_4)_2$, or $\text{Mg}(\text{NH}_4)_4(\text{PO}_4)_2$; the former is unchanged by ignition, and the latter gives magnesium metaphosphate, whereas the precipitate of normal composition is converted into magnesium pyrophosphate.

If the precipitation takes place in the presence of much potassium or sodium salt, the precipitate is contaminated with magnesium potassium (or sodium) phosphate. If much ammonium, potassium, or sodium salt is present, reprecipitation is essential. In any case, reprecipitation is desirable to procure the best results.

On heating to 100° , magnesium ammonium phosphate loses 5 molecules of water; above 200° it is converted into magnesium pyrophosphate.

Magnesium Pyrophosphate, $\text{Mg}_2\text{P}_2\text{O}_7$, is unchanged by ignition in air, but if ignited in contact with carbon above 900° , phosphorus is lost. Magnesium pyrophosphate melts at about 1300° .

Exercise.—Weigh accurately about 0.5 gram of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and transfer to a 350 ml. beaker. Dissolve in water, and determine the magnesium as follows.

Procedure.—To the solution of magnesium sulphate, containing not more than 0.1 gram of magnesium oxide, add 5 to 10 ml. of concentrated hydrochloric acid, and dilute to a volume of 125 to 150 ml. Add 1 ml. of methyl red, cool well, and add 10 ml. of a freshly prepared solution of diammonium hydrogen phosphate containing 25 grams of this salt to 100 ml. of water. Neutralise, while stirring, with ammonia (0.9 sp. gr., *i.e.* about 80 ml. of 0.880 ammonia made up to 100 ml. with water) added from a burette. Stir for five minutes, then add 5 ml. more of the ammonia solution, and stir for ten minutes. Allow to stand for four hours, or preferably overnight, and filter through close texture paper, washing the precipitate first by

decantation, and then two or three times on the filter with a solution of ammonia (5 ml. of 0.880 ammonia diluted to 100 ml.). Dissolve the precipitate on the filter with about 50 ml. of warm normal hydrochloric acid, and wash the paper thoroughly with hot very dilute (1 in 100) hydrochloric acid. Add methyl red, and about 1 ml. of the ammonium phosphate solution. Complete the precipitation as before. The final volume should be between 100 and 150 ml. Allow to stand for at least four hours.

(1) *If the precipitate is to be converted into the pyrophosphate for weighing*, filter off and wash the precipitate with ammonia diluted as above until a few drops of the filtrate give no turbidity with dilute nitric acid and silver nitrate. Dry the filter with the precipitate in the steam-oven, and incinerate the paper, apart from the precipitate, *at as low a temperature as possible* in the manner described on p. 245, using preferably a platinum crucible. If the paper is moistened with dilute ammonium nitrate, a white ash is more easily obtained eventually. The paper should not be allowed to take fire. After all volatile carbonaceous matter has been driven off, the residue may be ignited strongly with the lid open enough to allow circulation of air, until the residue is as white as possible. Add the precipitate, and ignite to constant weight at a temperature not exceeding 1100° . If a platinum crucible is being used, a good Bunsen flame will be adequate, but for a porcelain crucible the blowpipe is permissible.

From the weight of magnesium pyrophosphate obtained calculate the percentage of magnesium in magnesium sulphate.

(2) *If the precipitate is to be weighed as the hexahydrate of magnesium ammonium phosphate*, filter off on a Gooch or sintered glass crucible (porosity 3), and wash with ammonia diluted as above until a few drops of the filtrate give no turbidity with dilute nitric acid and silver nitrate. Wash finally either with three small portions of alcohol followed by similar treatment with ether, or with five small portions of acetone. In either case the crucible is then placed in an oven at 45° to 50° for half-an-hour, cooled, and the precipitate weighed as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$.

Determination of Magnesium by means of Oxine

The use of this reagent has been described under Aluminium (p. 316), and it may be conveniently employed in the determination of magnesium.

Procedure.—Weigh out accurately an amount of magnesium sulphate containing not more than 0.03 gram of magnesium. Dissolve it in about 100 ml. of water in a 250 ml. beaker. Add 2 grams of ammonium chloride, and 0.5 ml. of *o*-cresolphthalein indicator (0.02 per cent. alcohol), and then 6N ammonia solution in at least 5 ml. excess of that required to give the violet colour of the indicator (*pH* 9.5). Add *very slowly* from a burette, with constant stirring, a 2.5 per cent. solution of oxine in 4 per cent. v/v acetic acid (see p. 317) until a *small* excess is present as shown by a deep yellow colour in the supernatant liquid. One ml. of the oxine solution is required for each 1.9 mg. of magnesium present. Digest the precipitate for 10 minutes on the steam-bath, and filter it off on a sintered glass crucible, porosity 4, using the filtrate to transfer the precipitate to the filter. Wash the precipitate with 50 ml. of hot water. Dry at 105° or 160° for 1 hour, then for half-hour periods until constant weight is attained. The precipitate dried at 105° has the composition $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$; dried at 160° it has the composition $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2$. (See Miller and McLennan, *J. Chem. Soc.*, 1940, 656.)

Instead of the precipitate being dried and weighed, it may be dissolved in warm 2N hydrochloric acid and titrated with a bromate-bromide mixture as described under Aluminium (p. 317). In this case the volume of oxinate solution taken for titration should not contain more than 0.01 gram of magnesium. One ml. of decinormal bromate solution is equivalent to 0.304 mg. of magnesium.

MANGANESE

Manganese is usually determined volumetrically (p. 126) or colorimetrically (p. 302). The gravimetric methods are difficult and are not recommended.

In gravimetric analysis, manganese is always determined after removal of the metals precipitated in acid solution by hydrogen sulphide. Hillebrand, in his *Analysis of Silicate and Carbonate Rocks*, states that "the gravimetric determination of

manganese in small amount seems to be more of a stumbling-block to the average chemist than that of almost any other of the frequently occurring elements in mineral analysis. This is due almost always to incomplete prior precipitation of elements which later suffer coprecipitation with the manganese."

For the separation of iron and manganese see p. 351.

Forms in which Manganese is precipitated

Manganous Carbonate.—This method is applicable in the absence of other metals that form insoluble carbonates. Only the alkali metal and ammonium salts may be present.

Manganese Dioxide (Hydrated).—Precipitation in this form by means of ammonium persulphate provides a method of separation from chromium. If more than traces of zinc, nickel, or cobalt are present, a second precipitation is necessary for complete separation.

Manganese Sulphide.—In this form, manganese is precipitated by means of ammonium sulphide along with nickel and cobalt. The nickel and cobalt are removed by precipitation with hydrogen sulphide in presence of acetic acid and ammonium acetate.

Manganese Ammonium Phosphate.—On account of the general insolubility of phosphates, this method is of limited applicability, but the precipitate obtained is so easily filtered off that the method has marked advantages when no separation from other metals is required. The procedure is identical with that described for zinc in presence of alkalis (p. 407). Ammonium chloride is added prior to the precipitation, and the precipitate is converted into the pyrophosphate, $\text{Mn}_2\text{P}_2\text{O}_7$, by gentle ignition.

Determination of Manganese as Oxide after Precipitation as Carbonate

OUTLINE OF METHOD.—The manganese is precipitated as manganous carbonate by means of ammonium carbonate. By ignition, first in air and then in a current of carbon dioxide, the precipitate is converted into Mn_3O_4 , which is weighed; or it may be converted into and weighed in one or other of the forms mentioned below.

Manganous Carbonate is a buff-coloured powder which darkens somewhat on exposure to air and is sometimes difficult

to filter off. It is practically insoluble in water and in solutions of ammonium salts. It dissolves in acids and is slightly soluble in solutions of alkali carbonates.

At a high temperature, with access of air, manganous carbonate is converted mainly into Mn_3O_4 , together with traces of Mn_2O_3 and MnO_2 , the actual composition of the residue depending on the manner of ignition. This mixture of oxides may be converted into :—

- (1) MnO (green), by heating to a high temperature in a current of hydrogen ;
- (2) Mn_3O_4 (brown), by heating to a high temperature in a current of carbon dioxide ;
- (3) Mn_2O_3 (black), by heating to low redness in a current of oxygen ;
- (4) MnS (green), by heating with sulphur in hydrogen ;
- (5) MnSO_4 (white), by adding sulphuric acid and heating to low redness.

The first four procedures produce oxides of uncertain composition. If a gravimetric finish must be used it is best to convert the manganese into manganese ammonium phosphate and ignite this to the pyrophosphate (*cf.* magnesium, p. 359). Failing this, the manganese should be weighed as the sulphate.

Procedure.—If the manganese is present as permanganate it must first be reduced to a manganous salt by means of sulphur dioxide and the excess of sulphur dioxide expelled by boiling.

Neutralise the solution with ammonia, add 10 grams of ammonium chloride and a slight excess of ammonium carbonate. Allow the beaker to remain on a gently heated steam-bath until the precipitate has settled completely. Filter, and wash the precipitate with hot water. Incinerate the filter together with the precipitate in a crucible. Add sulphuric acid, evaporate to fumes, and finally ignite at a dull red heat. Weigh as MnSO_4 .

MERCURY

Mercury may be determined volumetrically by methods described on pp. 163 and 197, and also after precipitation as mercuric iodate (see p. 364).

For colorimetric methods, see for example Strafford and Wyatt, *Analyst*, 1936, **61**, 528; and Brumblay, *Anal. Chem.*, 1952, **24**, 905.

Forms in which Mercury is precipitated

Mercuric Iodate—The mercury must be present as mercuric nitrate or sulphate, but not as halide. This method does away with the need to remove sulphur carried down when mercury is precipitated as mercuric sulphide, but is not applicable when silver, lead, bismuth, or ferric iron is present.

Mercuric Sulphide.—The mercury must all be present as a mercuric salt. This method is recommended when applicable, *i.e.* in absence of those metals that are precipitated in a similar manner.

Mercury Zinc Thiocyanate.—This is a convenient method for determining mercuric mercury, but in addition to metals which give insoluble thiocyanates, bismuth, cobalt and nickel must be absent as they would be partially precipitated.

Metallic Mercury.—This method is useful for separating mercury from all other metals. It is applicable to mercury in any form of combination.

Determination of Mercury as Iodate

Mercury in the form of mercuric nitrate or sulphate, but not halide, can be determined as mercuric iodate which is precipitated when excess of iodic acid is added to a solution of the mercuric salt containing dilute nitric acid. The mercuric iodate is filtered off, and in the gravimetric method is weighed as such, whilst in the volumetric method the mercuric iodate is added to a solution of potassium iodide and after the addition of acid the liberated iodine is immediately titrated with a standard solution of sodium thiosulphate. This method is not applicable in presence of such metals as silver, lead, bismuth, and ferric iron, which are precipitated as iodates under the conditions described above, but moderate amounts of barium, strontium, and copper do not interfere (C. H. R. Gentry and L. G. Sherrington, *Analyst*, 1945, **70**, 419).

Exercise.—Determine the percentage purity of mercuric oxide.

Weigh out accurately 0.5 gram of mercuric oxide and dissolve it in dilute nitric acid in an evaporating basin.

Take to dryness on a water-bath, moisten the residue with 1 ml. of concentrated nitric acid, take up in 50 ml. of distilled water, and make up to 100 ml. in a standard flask.

For the gravimetric method, take 25 ml. of this solution in a 250 ml. beaker, add 1 ml. of concentrated nitric acid, and dilute to 100 ml. Heat the mixture to boiling, and add slowly and with vigorous stirring 2 grams of iodic acid dissolved in the least possible amount of hot water (2 to 3 ml. will suffice). Keep the mixture hot for 5 minutes, stirring occasionally, and then cool rapidly to room temperature; mercuric iodate will separate as a heavy white precipitate. Filter, using a porosity 4 sintered glass crucible. When all the precipitate has been transferred to the filter by means of water containing 1 per cent. of nitric acid and 2 per cent. of iodic acid, wash it five times with this liquid and finally three times with cold water. Dry at 140° for an hour and weigh as mercuric iodate, $\text{Hg}(\text{IO}_3)_2$.

For the volumetric method 10 ml. of the original mercuric solution are taken, and mercuric iodate precipitated as described above. Filter off on a pad of paper pulp and wash as already described. Place the pad with its precipitate in a 250 ml. stoppered flask and wash the funnel with a 10 per cent. solution of potassium iodide, the washings being added to the contents of the flask. Add a further 2 grams of potassium iodide, shake until any mercuric iodide which has been formed dissolves, and dilute to 100 ml. Add 0.5 gram of sodium bicarbonate followed by 4 ml. of concentrated hydrochloric acid, and titrate the liberated iodine immediately with standard sodium thiosulphate solution, using starch solution added near the end-point as indicator. Calculate the percentage purity of the sample of mercuric oxide.

One litre of normal sodium thiosulphate solution is equivalent to 16.72 grams of mercury.

Determination of Mercury as Sulphide

OUTLINE OF METHOD.—The mercury is precipitated with hydrogen sulphide in acid solution, and, after removal of any free sulphur by extraction with carbon disulphide, is weighed as HgS .

Mercuric Sulphide is inappreciably soluble in boiling dilute acids. It is slowly converted into mercury thionitrate and finally into soluble mercuric nitrate by boiling concentrated

nitric acid. It may be dried completely at 100° ; at higher temperatures it volatilises unchanged.

Procedure.—The mercury, if not already in the mercuric state, must be oxidised by boiling with concentrated nitric acid. The presence of nitric acid in the solution is objectionable, because it gives sulphur with hydrogen sulphide, but it is not permissible to remove it by evaporation with hydrochloric acid since mercuric chloride would be volatilised in the process.

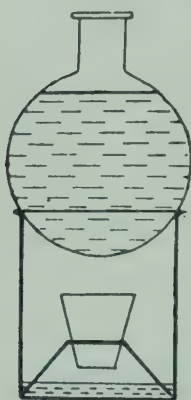


FIG. 70.

Saturate the cold solution with hydrogen sulphide, filter through a Gooch or sintered glass crucible, wash with cold water and then two or three times with alcohol. The sulphur in the precipitate is removed by extraction with carbon disulphide. Carbon disulphide usually contains some dissolved sulphur, and the following method of extraction is therefore recommended:—Place the crucible on a glass triangle within a beaker which contains some carbon disulphide. Cover the beaker with a flask containing cold water (see Fig. 70), and heat the beaker on the steam-bath. Within an hour all the sulphur will be extracted. Wash twice with alcohol to remove carbon disulphide, and dry at 100° to 110° . Weigh the HgS .

Determination of Mercury as Mercury Zinc Thiocyanate

OUTLINE OF METHOD.—The solution of the mercuric salt is treated with excess of a solution containing zinc sulphate and ammonium thiocyanate. The precipitated mercury zinc thiocyanate is collected in a sintered glass crucible, washed, dried, and weighed.

Mercury zinc thiocyanate is a white solid, very sparingly soluble in water. It is soluble in ammonium salts and in strongly acid solution. If the mineral acid concentration is greater than decinormal, it must be nearly neutralised with sodium hydroxide. If the mercury compound is not already in the mercuric state, it must be boiled with a little concentrated nitric acid, and the solution almost neutralised after dilution.

Procedure.—Weigh accurately about 0.25 gram of mercuric chloride into a 250 ml. beaker, add 75 ml. of water, and 1 ml. of dilute hydrochloric acid. While stirring vigorously add

25 ml. of the reagent, prepared by dissolving 3.9 grams of ammonium thiocyanate and 2.9 grams of zinc sulphate in water and diluting to 100 ml. A precipitate gradually separates, and it should be allowed to stand several hours or overnight before filtration. Filter off on a No. 3 sintered glass crucible, wash four times by decantation, using about 20 ml. portions of a washing liquid made by diluting 5 ml. of the precipitating reagent with 450 ml. of water. Transfer the precipitate to the crucible using this liquid in a wash-bottle, and finally wash the precipitate in the crucible three times with small amounts of water. Dry the precipitate in an air oven at 105° to 110° ; slight decomposition occurs at 120° . Weigh the $\text{HgZn}(\text{CNS})_4$.

Determination of Mercury as Metal

OUTLINE OF METHOD.—The dry substance is heated with a mixture of quicklime, iron filings, and lead chromate. The mercury that is driven off is collected and weighed.

Procedure.—A convenient apparatus is that devised by Penfield for the determination of water in minerals. Close a piece of glass tubing (about 20 cm. in length and 5 mm. in diameter) at one end, and blow bulbs at A and B (Fig. 71).

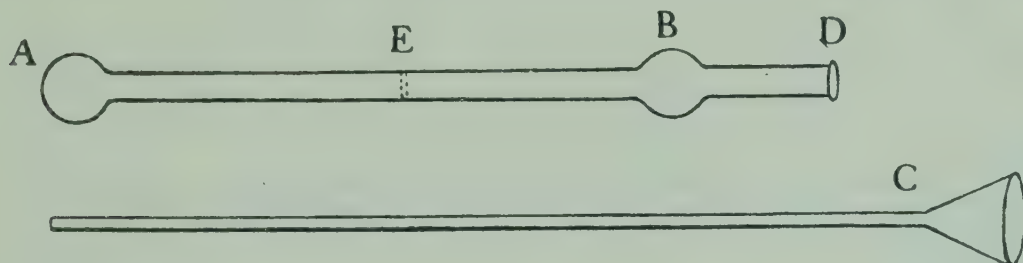


FIG. 71.

Clean, dry, and weigh the tube. By means of the long funnel C, introduce 0.5 to 1.0 gram of the powdered material into the bulb A. Weigh the tube and contents.

Add some iron filings by means of the funnel C, from which any adhering trace of the substance has meanwhile been removed. Mix the substance and filings thoroughly by rotating the tube. Then add a mixture of one part of quicklime, one part of powdered (fused) lead chromate, and two parts of iron filings, until about 8 cm. of the tube has been filled. Insert a small plug of asbestos, E, so that, after the tube has been tapped, only a very shallow air-channel remains over the mixture. Draw out the open end D into a fine capillary, as shown at F, Fig. 72.

Place the prepared tube in an iron tube that can be heated by a flat-flame burner. (A piece of iron gas-pipe about 15 cm. by 1.5 cm., closed at the ends with plugs of asbestos, may be used.) Wrap the bulb A in some asbestos paper to prevent it coming into direct contact with the iron tube; if this precaution is omitted, the bulb becomes hot before the narrow portion of the tube, and the mercuric salt is partly volatilised without decomposition. Place an asbestos shield at G, plug the gap in the shield with asbestos, and cover the bulb B with wet filter paper.

Heat the iron tube, at first with a small flame and at the end nearer G only. Gradually increase the flame and move it until the whole iron tube is heated to a low red heat. The

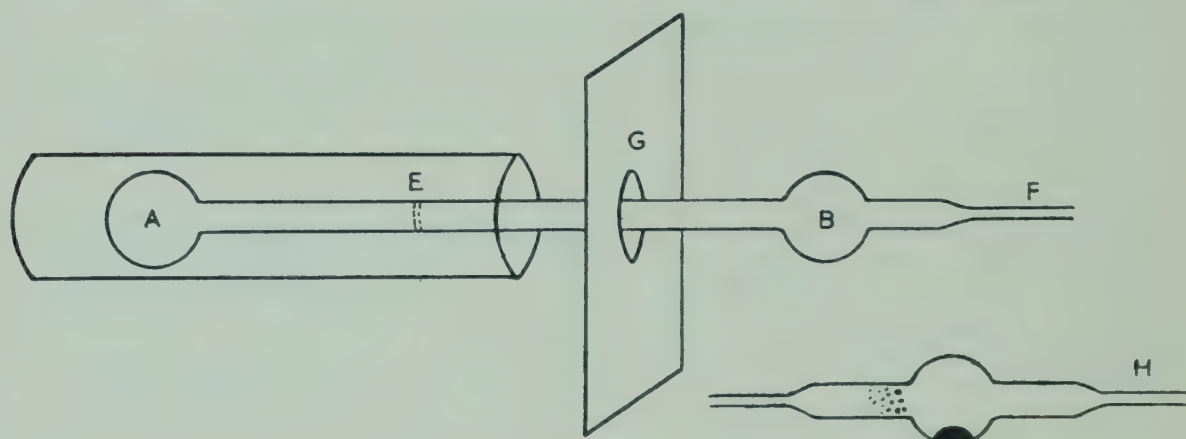


FIG. 72.

apparatus must be almost horizontal, but with the end F slightly lower than the closed end, so that, when the tube is gently tapped, any mercury that has condensed forms a globule and runs into the bulb B.

When all the mercury has distilled (usually within one hour), draw out the glass tube until the plug E is exposed. At the same time move the burner forward, so that the flame plays directly on the glass tube. As soon as the glass tube becomes red hot, draw it out and cut it off about midway between the plug E and the bulb B. The mercury is thus obtained in a tube, as shown at H, and is then weighed after removal of any water.

To remove water, draw a current of dry air through the tube until the weight is constant. Shake out the main portion of the mercury, and remove the remainder by blowing air through the gently heated tube. (**Caution.**—*Mercury vapour is poisonous.*) Weigh the empty tube after cooling.

MOLYBDENUM

Molybdenum may be determined volumetrically, but is more commonly determined by a gravimetric method.

A colorimetric method is described on p. 303.

Forms in which Molybdenum is precipitated

Molybdenum Sulphide.—This method involves the previous separation of tungsten if present, but vanadium does not interfere.

Mercurous Molybdate.—This is obtained by the addition of mercurous nitrate to a molybdate, a process similar to that used with a tungstate (p. 401). It requires, however, more care in conversion to the trioxide than is the case with mercurous tungstate, since molybdenum trioxide is more volatile than tungsten trioxide.

Lead Molybdate.—This compound may be precipitated in the presence of most of the metals, but vanadium and tungsten must be removed previously.

Molybdenum Salt of α -Benzoinoxime.—This constitutes the best method of determining molybdenum.

Determination of Molybdenum as Lead Molybdate

OUTLINE OF METHOD.—Lead molybdate is precipitated by the addition of lead acetate to a solution of ammonium molybdate containing ammonium acetate and acetic acid. The precipitate is filtered off, washed, ignited, and weighed.

Lead Molybdate, PbMoO_4 , is a white solid, insoluble in acetic acid, and unaltered by ignition even in contact with filter paper.

Procedure.—Weigh out accurately about 0.1 gram of ammonium molybdate. Dissolve it in about 200 ml. of water, add 15 ml. of 2N HCl, and 10 grams of ammonium acetate. Heat to boiling, and run in 10 per cent. lead acetate solution from a burette whilst stirring until no further precipitation takes place. About 5 ml. should be sufficient. Heat on the water-bath for a few minutes, and filter through ashless paper whilst hot. Wash with a hot 1 per cent. solution of ammonium acetate until the washings give no turbidity with potassium chromate. Dry the filter and ignite it in a porcelain crucible at as low a temperature as possible until all carbon has been burnt away. Cool, and weigh.

Determination of Molybdenum with α -Benzoinoxime

Procedure.—Obtain a solution containing 10 ml. of sulphuric acid and not more than 0.15 gram of sexivalent molybdenum in a volume of about 200 ml. Reduce any vanadate or chromate that may be present by adding sulphurous acid, and boil off the excess sulphur dioxide. Cool the solution to a temperature of less than 10° . Add slowly, while stirring, 10 ml. of a 2 per cent. solution of α -benzoinoxime in alcohol and 5 ml. more for each 10 mg. of molybdenum present. Add bromine water until the solution is pale yellow (to prevent any reduction of molybdenum) and add a few ml. more of reagent. Allow the mixture to stand for 10 to 15 minutes, add a little paper pulp, and filter through a close-texture paper. Wash the precipitate with cold water. If enough reagent has been added to ensure complete precipitation of the molybdenum, it will crystallise out in the filtrate. Transfer the paper and precipitate to a silica or platinum crucible, char the paper without allowing it to burst into flame, and finally ignite to constant weight in a muffle at 500 to 525° . The ignition product is MoO_3 .

NICKEL

Nickel is determined after removal of metals that are precipitated by hydrogen sulphide in acid solution. Although a pure nickel solution yields no precipitate with hydrogen sulphide in acid solution, some nickel is coprecipitated with the sulphides of the copper and arsenic group unless the solution is strongly acid.

Nickel can be determined volumetrically by the method described on p. 192.

A colorimetric method for the determination of traces of nickel is described on p. 303.

Forms in which Nickel is precipitated

Nickel Sulphide.—Ammonium monosulphide precipitates nickel, together with the other metals of the iron and zinc group, and this method serves to separate nickel, iron, zinc, etc., from the alkalis and alkaline earths. Nickel sulphide is not precipitated from acid solutions, but the precipitated sulphide dissolves very slowly in cold dilute acids.

Nickel Salt of Dimethylglyoxime.—Nickel is precipitated in this form from alkaline or acetic acid solutions by means of an alcoholic solution of dimethylglyoxime. This method separates nickel from cobalt, zinc, manganese, and (with appropriate modification) from iron, aluminium, chromium, and copper.

Metallic Nickel (Electrolytic).—This is a useful and accurate method for the determination of nickel. The method can be adapted to provide a separation of nickel from copper and other metals (see p. 273).

Determination of Nickel by the Dimethylglyoxime Method

OUTLINE OF METHOD.—The nickel is precipitated by adding dimethylglyoxime dissolved in alcohol to a hot, slightly acid solution, and then adding ammonia or sodium acetate. The precipitate is collected in a Gooch or sintered glass crucible, dried at 120° , and weighed as $(C_4H_7O_2N_2)_2Ni$.

Dimethylglyoxime,



is a white, crystalline substance, insoluble in water. The reagent is a 1 per cent. solution in absolute alcohol. It precipitates nickel as a voluminous, scarlet, crystalline salt, $(C_4H_7O_2N_2)_2Ni$, easily soluble in mineral acids, but practically insoluble in water, acetic acid, and dilute ammonia. It is soluble in solutions containing a high percentage of alcohol.

Procedure.—Dilute the solution (which should contain not more than 0.05 to 0.06 gram of nickel, and should be slightly acid) to 200 ml. and heat to about 80° . Add an excess of the reagent (20 to 30 ml.), and then add ammonia until the solution is very slightly alkaline (or add 2 to 3 grams of sodium acetate). Keep the solution hot for a few minutes, cool, and allow to stand for not more than an hour, filter through a Gooch or sintered glass crucible (porosity 2 or 3), and wash the precipitate with hot water. Dry at 120° for an hour, and weigh. The precipitate contains 20.32 per cent. of nickel.

If cobalt is present, dilute the solution before precipitation so that 200 ml. contain not more than 0.1 gram of cobalt, and add at least 50 ml. of the reagent for 0.05 gram of nickel.

If copper is present, add sufficient ammonia to form the blue, soluble cuprammonium salt before precipitating the nickel. Filter off and wash the precipitate. Dissolve it in hot nitric acid (1 : 3), and reprecipitate the nickel in presence of ammonia as before.

If zinc is present, add sufficient ammonium chloride to prevent precipitation of the zinc by ammonia.

If iron, aluminium, or chromium is present, add sufficient tartaric or citric acid (1 to 3 grams) to prevent their precipitation as hydroxides, dilute to 300 ml., and add a large excess of the reagent.

If manganese is present, add sodium acetate (not ammonia) to complete the precipitation of the nickel complex.

NITRATE

Volumetric methods for the determination of nitrate are described on pp. 110 and 122, and a gas-volumetric method on p. 487.

NITRITE

A volumetric method for the determination of nitrite is described on p. 121, and gas-volumetric methods on pp. 487 and 488.

OXALATE

Volumetric methods for the determination of oxalate are described on pp. 118 and 151.

Oxalate may be determined gravimetrically by an appropriate modification of the method described for calcium on p. 262, using a boiling solution of calcium chloride as precipitant.

PEROXIDE

Volumetric methods for the determination of peroxide are described on pp. 119 and 172, and a gas-volumetric method on p. 489.

PERSULPHATE

Volumetric methods for the determination of persulphate are described on pp. 113 and 129.

PHOSPHATE

A volumetric method for the determination of phosphate is described on p. 111, and a colorimetric method on p. 304.

Forms in which Phosphate is precipitated

Ammonium Phospho-molybdate.—The chief value of this method is that it is applicable in presence of the alkaline earth metals, aluminium, and iron.

Magnesium Ammonium Phosphate.—This method is not applicable in presence of metallic radicals other than the alkalis.

Determination of Phosphate by the Molybdate Method.

OUTLINE OF METHOD.—The phosphate is precipitated in presence of nitric acid by ammonium molybdate. The precipitate is collected in a Gooch or sintered porcelain crucible, ignited, and weighed as phospho-molybdic anhydride, $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$.

Ammonium Phospho-molybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot x\text{H}_2\text{O}$, is a bright yellow crystalline substance, insoluble in dilute nitric and sulphuric acids, but somewhat soluble in hydrochloric acid. It is readily soluble in ammonia, and soluble also to some extent in solutions containing chlorides or ammonium salts (except the nitrate).

It may be weighed as the anhydrous salt after drying at 180° , but it is better to convert it into phospho-molybdic anhydride, $24\text{MoO}_3 \cdot \text{P}_2\text{O}_5$, by gentle ignition. The anhydride must not be heated too strongly, otherwise phosphoric anhydride will be volatilised and lost. Ammonium phospho-molybdate may also be determined indirectly by an alkalimetric method (p. 111).

On account of the small proportion of phosphorus in the final precipitate, an amount of substance containing about 10 mg. of P_2O_5 is ample for an analysis.

The following solutions are required :—

(1) *Ammonium Molybdate.*—Dissolve 3 grams of the powdered crystals in 100 ml. of water.

(2) *A Washing Solution* containing 50 grams of ammonium nitrate and 40 ml. of concentrated nitric acid per litre of water.

Preparation of a Solution for Analysis.—As a rule, all the phosphorus can be obtained in solution by boiling the substance with concentrated nitric acid. For complex rocks containing

silicates, however, fusion with sodium carbonate is necessary, and the silica must be removed by evaporation to dryness in presence of nitric acid.

The phosphorus must be in the form of ortho-phosphate; meta- or pyro-phosphates must therefore be boiled with dilute nitric acid for a few minutes.

Procedure.—Place a measured volume of the phosphate solution, containing about 10 mg. of P_2O_5 , in a 400 ml. beaker, add 10 grams of ammonium nitrate, and 5 ml. of concentrated nitric acid. Add water to give a final volume of about 100 ml. Measure 50 ml. of the 3 per cent. ammonium molybdate solution into a flask. Heat the two solutions to between 40° and 45° , and add the ammonium molybdate solution slowly to the phosphate mixture, using a dropping-tube (p. 261). Stir continuously for a few minutes, but avoid touching the sides of the beaker with the stirring-rod. After about twenty minutes, filter through a Gooch or sintered porcelain crucible, and wash with 60 to 80 ml. of the prescribed washing solution.

Place the crucible inside a larger metal crucible in which a perforated porcelain disc is first placed. Heat the outside crucible very carefully to dull redness until the precipitate has a uniform greenish-black colour. Weigh the phospho-molybdic anhydride, one gram of which contains 0.03947 gram of P_2O_5 . The anhydride is rather hygroscopic.

Determination of Phosphate as Magnesium Pyrophosphate, after Precipitation as Magnesium Ammonium Phosphate

OUTLINE OF METHOD.—The phosphate is precipitated by addition of “magnesia mixture” as magnesium ammonium phosphate, which is converted by ignition into magnesium pyrophosphate, $Mg_2P_2O_7$.

Magnesium Ammonium Phosphate, $MgNH_4PO_4$.—The properties of this precipitate and the conditions under which it may be obtained pure, are described on p. 359. The precipitate has the composition corresponding to the normal salt, $MgNH_4PO_4$, only when these conditions are rigidly adhered to.

Magnesium Pyrophosphate, $Mg_2P_2O_7$, has already been described (p. 359).

Procedure.—To a neutral or weakly acid solution of an ortho-phosphate, containing not more than 0.1 gram of P_2O_5 , add 5 ml. of concentrated hydrochloric acid, and 1 ml. of methyl

red indicator. Dilute the solution to 150 ml., and add 10 ml. of a solution prepared by dissolving 5 grams of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 10 grams of NH_4Cl in water, adding 5 ml. of normal hydrochloric acid, and diluting to 100 ml. After adding the magnesia solution, cool well, and stir while neutralising with ammonia. The procedure from this stage is the same as that described under the determination of magnesium (p. 359), except that when the reprecipitation from the hydrochloric acid solution is carried out, 2 ml. of the "magnesia mixture" are added instead of 1 ml. of ammonium phosphate solution.

PLATINUM

Platinum when alloyed with gold or silver is usually determined by a dry assay involving cupellation. If other metals of the platinum group are present, the process of its determination is complex. In either of these cases special books must be consulted.

Forms in which Platinum is precipitated

Ammonium Chloroplatinate, $(\text{NH}_4)_2\text{PtCl}_6$. This is a yellow, crystalline, sparingly soluble compound, 100 grams of water dissolving 0.7 gram at 10° . It is almost insoluble in alcohol. It may be weighed as such, or it may be ignited and the resulting metallic platinum weighed. The former procedure is preferable, as platinum may be lost during the combustion of the filter paper owing to the formation of a volatile compound of platinum chloride and carbon monoxide.

Metallic Platinum.—This is obtained by reduction with magnesium and dilute hydrochloric acid, or with formic acid.

Platinum Sulphide, PtS_2 .—This is precipitated by hydrogen sulphide from a solution of chloroplatinic acid. It is soluble in yellow ammonium sulphide. It gives metallic platinum upon ignition.

Determination of Platinum as Ammonium Chloroplatinate

OUTLINE OF METHOD.—A solution of chloroplatinic acid is treated with ammonium chloride solution and alcohol, and the ammonium chloroplatinate precipitated is filtered off on a Gooch or sintered glass crucible, and weighed.

If the determination is to be made on a sample of metal which has only small amounts of impurity, weigh 0.05 to 0.1 gram into a small porcelain dish. Add 10 ml. of concentrated hydrochloric acid and 3 ml. of concentrated nitric acid, cover the dish, and heat on a water-bath. Add more acid if the metal does not dissolve completely. Evaporate as far as possible on the water-bath, cool, and add 3 ml. of concentrated hydrochloric acid. Evaporate again as far as possible, and repeat the treatment in order to ensure complete removal of nitric acid.

If the determination is to be made on a solution of chloroplatinic acid, measure out an amount containing 0.05 to 0.1 gram of platinum into a small porcelain dish, and evaporate as far as possible on a water-bath.

Dissolve the residue in the dish in about 1 ml. of water, add one or two drops of dilute ammonia until the liquid just smells of it, and then make the liquid just acid with dilute hydrochloric acid. Add excess (1 to 2 ml.) of ammonium chloride solution, and 15 ml. of industrial alcohol. Cover the dish with a watch-glass, place over it an inverted beaker, and leave it standing overnight in a cool place. Transfer the precipitate to a Gooch or sintered glass crucible with 80 per cent. alcohol, using a rubber-tipped rod to assist the operation. Wash the precipitate with 80 per cent. alcohol until 1 ml. of the filtrate leaves no residue when evaporated. Finally, wash with acetone, and dry in an oven at 60°. Cool and weigh as $(\text{NH}_4)_2\text{PtCl}_6$.

If the chloroplatinic acid to be determined contains considerable amounts of impurity, it is advisable to reduce the platinum to the metallic state by the addition of magnesium to the acid solution. The completion of the precipitation may be judged by the disappearance of the yellow colour. Filter the solution, wash the metallic platinum, and ignite with the filter in a small dish. After cooling, dissolve in aqua regia and determine the platinum as described above.

POTASSIUM (AND SODIUM)

Potassium and sodium usually occur together. Lithium also is often present, and in this case the lithium must first be separated from the potassium and sodium as described on p. 356. Either sodium or potassium may be determined in the

presence of small amounts of the other metal by a direct method. Alternatively both may be weighed together as chlorides, and either metal determined directly, the other being found by difference.

The preliminary extraction of sodium and potassium in an insoluble silicate is described on p. 445.

Potassium may be determined by flame photometry (see p. 510).

Forms in which Potassium is precipitated

Potassium Chloroplatinate.—Ammonium salts and all metals other than sodium and potassium must be removed. Sulphate and phosphate must also be removed.

Potassium Perchlorate.—The special advantages of this method are that the use of expensive platinum salts is avoided, and that it is applicable in presence of phosphate and of most metals. The only common acidic radical that must be removed is sulphate. Ammonium salts must be removed.

Dipotassium Sodium Cobaltinitrite.—This method is sometimes useful because it is applicable in presence of sulphate, but it is less accurate than the two previous methods. Ammonium salts must first be removed.

Potassium Tetraphenyl Boron.—Sodium tetraphenyl boron is a specific reagent for potassium and ammonium ions in the presence of decinormal mineral acid. Mercuric ions should, however, be absent. This method is the best gravimetric one for potassium.

Preparation of a Solution for Analysis

(1) *In the Complete Analysis of a Mixture*, all other metals, including lithium, must be removed prior to the determination of sodium and potassium. (See Lithium, pp. 356 and 357.) If other metals are absent, but any sulphate or phosphate is present, add barium hydroxide solution in slight excess and, without filtration, evaporate to about 50 ml. Add a few drops of freshly prepared ammonium carbonate solution in order to precipitate the barium excess, filter through a small filter paper, and wash with hot water. Determine the sodium and potassium in the filtrate.

(2) *If only Potassium is to be determined*, extract a weighed sample of the original material with hot, dilute hydrochloric acid, and filter from any insoluble matter. (With many minerals, particularly silicates, it is not possible to bring the potassium into solution by treatment with hydrochloric acid. The procedure for a case of this kind is described on p. 445.) Evaporate the solution of mixed chlorides to dryness in a porcelain basin, and heat on a sand-bath to barely visible redness for about fifteen minutes, in order to convert iron, aluminium, etc., into insoluble basic salts. The duration of the ignition should be such that, on extracting the residue with water, a colourless solution, free from iron, is obtained.

When sulphate is present, it must be removed (except for the cobaltinitrite method) after the evaporation to dryness and extraction, by adding a slight excess of barium hydroxide solution, and completing the evaporation and ignition as described above.

Extract the soluble alkali salts by repeated treatment with boiling water, breaking up the insoluble residue as much as possible with a glass rod. Filter into a glass evaporating basin, and determine the potassium by the perchlorate method.

Determination of Potassium as Chloroplatinate

OUTLINE OF METHOD.—After removal of sulphate, phosphate, ammonium salts, and all metals other than sodium and potassium, hydrochloroplatinic acid is added, and the solution is evaporated to dryness. The residue is extracted with methyl alcohol, which dissolves the sodium chloroplatinate. The insoluble residue of potassium chloroplatinate is dried and weighed.

Potassium Chloroplatinate, K_2PtCl_6 , is a golden-yellow, crystalline salt. It is sparingly soluble in water, and nearly insoluble in methyl alcohol and in ethyl alcohol. At 20° , 100 grams of each of these solvents, in the order named, dissolve 770 mg., 2.7 mg., and 1 mg. The precipitate obtained in quantitative analysis is, after washing and drying, not pure K_2PtCl_6 ; it is, however, of constant composition, if the working conditions are always the same. If the procedure described below is adopted, the precipitate contains 16.02 per cent. of potassium (calculated for K_2PtCl_6 , $K = 16.08$ per cent.).

se. As ammonium chloroplatinate is also insoluble in alcohol, p. 356, essential to remove all ammonium salts prior to the pre-

cipitation, and also to guard against contamination of the solution by ammonia from the laboratory atmosphere during the analysis.

Sodium Chloroplatinate, $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, is an orange-red salt which is soluble in absolute ethyl alcohol, somewhat more soluble in absolute methyl alcohol, and readily soluble in water. The hydrated salt becomes anhydrous at the temperature of the steam-bath. The anhydrous salt is less soluble in absolute alcohol than the hydrated salt. In order to separate sodium and potassium chloroplatinates, it is best to use absolute *methyl* alcohol.

Procedure.—The solution, after removal of sulphate, phosphate, and all metals other than sodium and potassium is evaporated to dryness. The sodium and potassium are obtained finally in a platinum crucible as pure chlorides, and weighed. Full details of the procedure up to this stage are given on p. 384. The potassium is then determined as chloroplatinate, as follows :—

Dissolve the mixed chlorides in 5 ml. of water and transfer the solution, with the rinsings of the crucible, to a small porcelain basin.

Both the sodium and potassium chlorides must be converted into chloroplatinates, because sodium chloride is insoluble in alcohol. In order to calculate the amount of hydrochloroplatinic acid required to effect this, the assumption is made that the whole of the chloride is *sodium* chloride. Since the reagent contains 10 per cent. of platinum (see p. 515), 1.7 ml. is required for 0.1 gram of sodium chloride, and the volume of reagent required is found by multiplying the weight of the mixed chlorides by 17.

To the solution of the mixed chlorides add 0.3 ml. more than the calculated quantity of hydrochloroplatinic acid, and place the basin on the steam-bath. If necessary, add more water to dissolve any precipitated potassium chloroplatinate that may remain after the solution has become warm. Evaporate until the liquid is syrupy and becomes solid on cooling.

Add about 5 ml. of absolute methyl alcohol ¹ to the residue and break up the mass thoroughly with a platinum spatula or glass rod. Decant the liquid through a Gooch or sintered glass

¹ Although less satisfactory, 95 per cent. ethyl alcohol (by volume) may be used.

crucible that has been dried at 160° and weighed. The solid must be kept as far as possible in the basin, only the clear liquid being poured into the filter. Repeat this treatment with successive *small* quantities of methyl alcohol (grinding up the precipitate each time as thoroughly as possible) until the filtrate is colourless. Transfer the precipitate to the crucible. Wash the sides of the crucible five or six times with small quantities of alcohol, drain off the alcohol thoroughly, dry at 160° , and weigh.

The weight of the precipitate multiplied by 0.1602 gives the weight of potassium, and multiplied by 0.3055 gives the weight of potassium chloride.

Determination of Potassium as Perchlorate

OUTLINE OF METHOD.—The solution of mixed chlorides is evaporated almost to dryness with perchloric acid. All salts other than potassium perchlorate are then extracted with alcohol, and the insoluble residue is weighed.

Potassium Perchlorate, KClO_4 , is a sparingly soluble, crystalline salt. At 25° , 100 grams of water dissolve 2.08 grams of the salt, 100 grams of 99 per cent. alcohol dissolve 19 mg., and 100 grams of 98 per cent. alcohol containing 0.2 per cent. of perchloric acid dissolve 10 mg. The solubility decreases rapidly with falling temperature, and 100 grams of the last-named solvent at 10° dissolve only about 3 mg. The salt may be dried without decomposition above 100° and below 200° .

Sodium Perchlorate is a white salt which is readily soluble in water and alcohol.

Danger.—Serious explosions have occurred as the result of improper use of perchloric acid. Even the dilute acid must *not* be heated with organic matter, and cases have been reported of explosions occurring in the cold with concentrated solutions of perchloric acid and organic matter. For a fuller account of the uses and dangers of perchloric acid, see Smith, G. F., *Analyst*, 1955, 80, 16.

Procedure.—To the solution of the mixed potassium and sodium chlorides, add 10 ml. of 20 per cent. perchloric acid. (If the mixed chlorides weigh less than 0.2 gram, 5 ml. may be sufficient.) Evaporate the solution, in a quartz or “resistance” glass basin, *almost* to dryness. The evaporation is performed on a sand-bath or, preferably, on a shallow sand-bath

tray covered with a set of rings. Add another 5 ml. of perchloric acid and again evaporate practically to dryness. If copious evolution of perchloric acid (white fumes) is not observed towards the end of the evaporation more acid must be added and the evaporation repeated. (The amount of perchloric acid used must be more than sufficient to convert all the salts into perchlorates.)

Prepare two washing solutions as follows:—(A) Add 0.3 ml. of 60 per cent. perchloric acid to 100 ml. of "absolute" alcohol; for this solution make a special "wash-bottle" from an ordinary test-tube—the outlet tube and *fine* jet being made from a single piece of glass tubing. (B) Saturate 100 ml. of rectified spirit with potassium perchlorate; the alcohol and perchlorate crystals must be vigorously shaken in a stoppered bottle for several minutes immediately before a portion is decanted or filtered for use.

Prepare a Gooch crucible—using somewhat more asbestos than usual—or a sintered glass crucible and fit the adapter into a filter-tube (a test-tube with side-tube) instead of the usual filter-flask.

To the almost dry, *cold* residue add 10 ml. of washing solution (A), stir well with a flat-ended glass rod and set aside for about five minutes with occasional stirring. Allow the potassium perchlorate to settle, and decant through the crucible. *Do not heat or explosion may occur.* (Reject the filtrate.)

Dissolve the perchlorate in the minimum amount of hot water,¹ and evaporate to dryness on the steam-bath. *Cool thoroughly*, add 10 ml. of washing solution (A), stir, and decant through the filter. Transfer the perchlorate to the crucible with the minimum amount (10 to 20 ml.) of the washing solution (A). Remove with a rubber-tipped rod (p. 43) the perchlorate adhering to the side of the basin; this requires special care, because it is not easily seen while the basin is wet. Finally, wash the filter five or six times by running into it from a small pipette successive portions (3 ml.) of washing solution (B). The total volume of the filtrate (excluding the initial 10 ml. rejected) should not exceed 40 to 50 ml.

Dry for one hour at 130° to 150°, cool, and weigh. Wash again with 2 to 3 ml. of washing solution (B), dry, and weigh.

¹ This is omitted if sodium is absent.

Determination of Potassium as Dipotassium Monosodium Cobaltinitrite

OUTLINE OF METHOD.—The solution containing potassium and sodium chlorides (nitrates or sulphates) is evaporated to dryness with an excess of sodium cobaltinitrite. The residue is extracted with acetic acid, washed with water, dried, and weighed.

Dipotassium Monosodium Cobaltinitrite,



is a lemon-yellow, crystalline salt, very sparingly soluble in water and in dilute acetic acid. The monohydrate is stable at 100°. The precipitate only has the above composition when the atomic ratio of sodium to potassium is greater than 22 : 1 during precipitation.

The sodium cobaltinitrite reagent is prepared as follows:—Dissolve 28 grams of cobalt acetate in a mixture of 75 ml. of water and 25 ml. of glacial acetic acid, and add a solution of 55 grams of sodium nitrite in 100 ml. of water. Warm the mixture gently in a round-bottomed flask and evacuate the flask to remove oxides of nitrogen. Set the solution aside for twenty-four hours. (A slight yellow precipitate usually separates because sodium nitrite is rarely free from potassium salts.) Filter, and dilute the solution to 250 ml. The solution should be kept in the dark.

Procedure.—To the solution of the mixed potassium and sodium salts (containing, preferably, not more than 0.1 gram of the potassium salt), add an excess of the reagent (not less than 20 ml.) and evaporate to dryness on the steam-bath. After cooling, stir the residue with 5 per cent. (approximately normal) acetic acid, allow the precipitate to settle, and decant through a Gooch or sintered glass crucible. Wash the precipitate by decantation with acetic acid, transfer it to the crucible, and wash with cold water until free from acid. Dry at 100°, and weigh as $\text{K}_2\text{NaCo}(\text{NO}_2)_6 \cdot \text{H}_2\text{O}$.

Determination of Potassium as Potassium Tetraphenyl Boron

Magnesium, calcium, aluminium, iron, cobalt, nickel, manganese, copper, sulphate, and phosphate do not interfere in the determination of potassium by this method. Ammonium and mercuric salts must be absent.

Procedure.—Obtain a solution containing about 10 mg. of potassium in 20 ml. Adjust the pH to about 4 to 5 by use of a suitable indicator and addition of acetic acid or alkali. Warm the solution to 40 or 50° and slowly add a 3 per cent. aqueous solution of sodium tetraphenyl boron that has been filtered perfectly clear. The reagent should be added in such an amount that the concentration of the excess after precipitation is about 0.2 per cent. Allow the precipitate to stand for 10 minutes, stirring it frequently during this period to prevent caking of the precipitate and supersaturation phenomena. Cool the solution in ice-water to less than 20° before filtration. Filter off on a sintered glass crucible, porosity 4, and wash with the minimum of wash-liquid (50 ml. should be adequate; the filtrate can be used if necessary to transfer the precipitate to the filter). The wash-liquid is cold water containing 3 ml. of reagent solution and 0.5 ml. of acetic acid per 100 ml. Finally wash with three or four 1 ml. portions of distilled water to remove the wash-liquid. The precipitate is more soluble in water than in the wash-liquid recommended; usually there is a compensation of errors arising from reagent held by the precipitate and from precipitate dissolved under the stipulated washing conditions (see Geilmann and Gebauhr, *Z. anal. Chem.*, 1953, **139**, 161). Dry the precipitate at 120 to 125° to constant weight.

Determination of Potassium and Sodium

OUTLINE OF METHOD.—All metals other than sodium and potassium, and all acid-radicals other than chloride, are removed (see p. 356). The solution is evaporated to dryness, and the residue of mixed chlorides weighed. The potassium is then determined by a suitable method and the sodium found by difference. Alternatively, if the content of potassium is known to be low, the sodium may be determined by means of zinc uranyl acetate (p. 391).

Sodium Chloride though readily soluble in water is almost insoluble in alcohol. It may be dried completely at 100°, but unless the drying process is very prolonged, it mechanically retains a trace of water which is expelled, with decrepitation, at higher temperatures. Heated to dull redness it melts, and at a bright red heat volatilises rapidly; at all temperatures above the melting-point there is appreciable loss by volatilisation.

Potassium Chloride very closely resembles sodium chloride in properties, but is slightly more volatile.

Procedure.—Evaporate the solution (from which sulphate, phosphate, and all other metals, including lithium, have been removed) in a porcelain basin until the bulk is reduced to about 50 ml. Transfer it to a 100 ml. platinum basin and rinse the porcelain basin with hot water. Evaporate to complete dryness on the steam-bath. (The subsequent manipulation is facilitated if the residue is dried at this stage as completely as possible, and it is advisable to heat the covered basin in an air-oven at 120° to 150° for an hour or more.)

Place the basin on a sand-bath and heat—very gently at first—until all moisture is driven off. During this operation, the basin must be kept covered with a clock-glass and the heating interrupted whenever decrepitation begins. When decrepitation has wholly ceased, raise the temperature, but do not remove the clock-glass. Continue the heating until the clock-glass and the sides of the basin are thickly coated with ammonium chloride.

Remove the clock-glass. Invert it and heat it gently over a small flame until all the ammonium chloride has volatilised, and set it aside to be washed later.

Place the basin on a pipe-clay triangle, and heat the sides of the basin until the ammonium chloride has volatilised. The burner must be held in the hand and the flame kept in constant motion to prevent over-heating and consequent volatilisation of any alkali chloride. Next heat the bottom of the basin in the same manner until no more ammonium chloride is given off. During this process the residue almost invariably blackens because of the charring of traces of organic impurities from the reagents.

Cool, add about 5 ml. of hot water, and filter through a very small ($5\frac{1}{2}$ -cm.) filter paper into a tared platinum crucible. *Extreme care is necessary at this stage, since the loss of a single drop of the solution renders the determination valueless.* Wash the basin and filter paper with hot water, using about 2 ml. for each washing. Wash into the crucible also any trace of salt adhering to the clock-glass.

Add one drop of hydrochloric acid and evaporate to complete dryness on the steam-bath. When the residue is apparently dry, remove from the steam-bath and heat the covered crucible

with a small flame, observing the same precautions as before against over-heating. Cool, and weigh. Repeat the heating until the weight is constant. (The salt is sometimes dark in colour on account of traces of carbon. The carbon will disappear on prolonged heating, but its weight is negligible.) The weight gives the amount of potassium and sodium chlorides.

Determine the amount of potassium in the mixed chlorides by following the instructions given on pp. 378, 380, 382, or 383, according to the method employed.

Calculate the weight of potassium chloride corresponding to the weight of the chloroplatinate, perchlorate, cobaltinitrite, or tetraphenyl boron salt obtained. Subtract the weight of potassium chloride from that of the mixed chlorides in order to find the weight of sodium chloride.

An alternative method consists of dissolving the weighed mixed chlorides in water, and determining the total chloride gravimetrically (p. 255). The weight of potassium chloride (x grams), and that of the sodium chloride (y grams), can then be calculated from the equations :—

$$x + y = \text{weight of mixed chlorides,}$$

$$\frac{35.46}{74.56} x + \frac{35.46}{58.46} y = \text{weight of total chlorine.}$$

The method is not very accurate, as any error in the determination of the total chlorine is multiplied by a large factor in calculating the values of x and y .

SILICA AND SILICATES

Properties of Silica.—From the analytical point of view, one may distinguish between three varieties of silica : (1) the jelly obtained by the incomplete dehydration of precipitated “silicic acid” ; (2) silica obtained by the ignition of precipitated “silicic acid” ; (3) native silica.

Gelatinous “silica” is readily soluble in alkali hydroxides and carbonates, and appreciably soluble in water and in acids. After ignition, it is practically insoluble in water and in acids (except hydrofluoric acid), but dissolves slowly in alkalis. Native crystalline silica (*e.g.* quartz) is insoluble in acids (except hydrofluoric acid), and is only slowly attacked by alkalis.

The powder obtained by drying gelatinous silica at 100° contains about 13 per cent. of water. Even at 200° , it still retains about 5 per cent.; only on ignition is the last trace of water expelled. The silica obtained by drying the jelly at 100° dissolves to an appreciable extent in acid, and is not rendered completely insoluble (as is often stated) by repeated evaporation to dryness with hydrochloric acid.

Precipitated silica is hygroscopic unless it has been ignited for at least twenty minutes with a blowpipe or a Méker burner.

A colorimetric method for silicon has been described on p. 305. An excellent rapid volumetric method for the determination of silica in silicates has been described by Wilson, *Analyst*, 1949, **74**, 877. This method is strongly recommended. The silicon is converted into silicomolybdic acid which is precipitated as quinoline silicomolybdate. This complex is dissolved in an excess of standard alkali, and the excess is back-titrated with standard acid.

Determination of Silica in an Insoluble Silicate

OUTLINE OF METHOD.—The silicate is decomposed by fusion with sodium carbonate or fusion mixture. The fused mass, after cooling, is disintegrated by warming with dilute hydrochloric acid, and the solution is evaporated to dryness on the steam-bath. The residue is dehydrated by baking in an air-oven. Hydrochloric acid and water are added, and the silica, most of which remains insoluble, is separated by filtration. The solution, which still contains a little silica, is evaporated to dryness again, and the residue is treated as before. The silica is then dehydrated by ignition and is weighed as SiO_2 .

Procedure.—In a small weighing-bottle place from 0.9 to 1.1 gram of the finely powdered silicate, and weigh accurately. Transfer the powder to a platinum crucible containing about 3 grams of pure, dry sodium carbonate, or fusion mixture. (Reweight the weighing-bottle to find the weight of silicate taken.) Add to the crucible another 3 grams of sodium carbonate or fusion mixture. Place the crucible on a sheet of glazed paper and mix the contents very thoroughly by stirring gently with a small spatula (preferably of platinum), care being taken that no unmixed silicate remains at the bottom of the crucible.

Cover the crucible, place it on a triangle about 4 inches above a small Bunsen flame, and heat gently for about five

minutes. Then lower the crucible and increase the flame gradually so as to melt the contents without any spluttering. Cautiously lift the lid of the crucible at intervals and examine the contents to make sure that there is no excessive frothing. No spatter should be seen on the lid if the fusion has been properly conducted. After heating until a state of quiet fusion is attained, heat more strongly with a Méker burner for about fifteen minutes. When the fusion is complete, the molten mixture may not be perfectly clear, but practically no further escape of gas bubbles should be seen. The whole operation takes from thirty to forty minutes.

Now lift the crucible with platinum-tipped tongs (p. 236) and impart a rotary motion to the vessel as cooling proceeds. In this way, the mixture is made to solidify in a thin sheet on the side and bottom of the crucible, and its subsequent removal from the crucible is thereby facilitated. As a rule the cold cake has a bluish-green colour owing to the presence of sodium manganate. It is easier to separate the melt if a Palau¹ crucible is used.

After the crucible has become *quite cold*, half-fill it with water and warm *cautiously* with a very small flame for several minutes; this will often suffice to loosen the cake. Transfer the liquid and the cake to a 15-cm. porcelain basin containing 150 ml. of hot water, and carefully rinse the crucible into the basin to remove as far as possible any adhering portions of the cake. Set the crucible and lid aside for final cleaning at a later stage. If the cake cannot be readily loosened in this way, place the crucible on its side in the porcelain basin together with 150 ml. of hot water, and warm on the steam-bath until the mass is completely detached from the crucible. Remove the crucible, rinse it carefully, and set aside with the lid for final cleaning. Break up the cake as far as possible with a blunt glass rod and then add, very gradually, excess of hydrochloric acid (20 ml. of concentrated acid mixed with 10 ml. of water), the basin being covered with a clock-glass to prevent loss during the decomposition of the carbonate.

When the disintegration is complete and effervescence has ceased, remove the clock-glass, rinsing it into the basin. Clean the crucible and the underside of the lid with a few drops

¹ Palau is an alloy of palladium and gold. It dissolves slightly in hot concentrated sulphuric acid.

of warm hydrochloric acid and add the rinsings of both to the basin. Evaporate to dryness on the steam-bath. Towards the end of the evaporation, stir frequently in order to break the crust that forms on the surface of the liquid. When the mass is quite dry, heat the basin in an air-oven between 105° and 110° for one hour in order to dehydrate the silica. This is then almost wholly insoluble in acid and the second evaporation of the solution—indicated below—may be omitted except in analyses of the highest accuracy.

Moisten the dry powder with 10 ml. of concentrated hydrochloric acid, stir, and set aside for ten minutes in order that any basic salts (of iron, etc.) may be converted into normal chlorides. Then add about 30 ml. of water and heat on the steam-bath and stir frequently until only the silica remains undissolved. The silica is often in a coarse condition and may be ground finer with a blunt glass rod.

Filter through a 9-cm. paper. Wash the silica several times by decantation with hot dilute acid. (The acid is not put into the wash-bottle but a little is added to the basin with each portion of hot water.) Transfer the silica to the filter. Remove any silica adhering to the basin and stirring-rod with a small piece of filter paper and add this to the main precipitate. Then wash the precipitate and paper with hot water until a few drops of the washings give no turbidity with silver nitrate.

Some of the silica always dissolves in the hydrochloric acid—probably only a fraction of 1 per cent. of the total silica if the above procedure is followed—and most of this may be recovered by evaporating the filtrate again to complete dryness. The residue is treated with acid, water is added, and the solution filtered through another (smaller) paper. The basin and the filter are washed with hot dilute acid and then with hot water as before.

Incinerate the filter papers containing the silica, without previous drying, in a weighed platinum crucible, and heat gently until all the carbon has been burnt away. Then ignite the silica in the covered crucible with the full flame of a Méker burner for at least twenty minutes. Cool, and weigh the SiO_2 . Repeat the ignition until constant weight is attained.

The silica obtained in this way is never entirely free from impurities, and it is advisable to determine the amount of impurity by driving off the silica with hydrofluoric acid and

weighing the non-volatile residue. To accomplish this, moisten the silica with water, add one or two drops of concentrated sulphuric acid, and 4 to 5 ml. of hydrofluoric acid.¹ (**Caution:** see footnote.) Evaporate to dryness, first on the steam-bath and then with a Bunsen flame (see p. 37 and Figs. 13 and 14). Ignite for two or three minutes with a Méker burner, cool, and weigh.

Pure silica should leave no residue, and the weight of the impurity must therefore be subtracted from the weight of the crude silica. The residue usually contains oxides of aluminium, iron, titanium, and phosphorus, and it may weigh from 2 to 10 mg. If a complete analysis of the silicate is being made, the subsequent precipitate of alumina, etc., should be ignited in the crucible containing the impurity found in the silica.

Notes.—(1) The evaporations for the removal of silica must be continued until the residue forms a *dry powder*. This powder is often very light, and, like ignited silica, is very easily blown away if care is not taken to protect it from draughts.

(2) In accurate work, the weight of the crude silica should always be corrected for impurity. If, however, it is not intended to determine the silica which, in spite of all the precautions described above, escapes precipitation and is found along with the ferric oxide and alumina (see p. 444), the correction should not be applied; instead, the assumption is made that the weight of the impurity is equal to that of the silica which has passed into the filtrate.

(3) The hydrofluoric acid must be free from non-volatile impurities. The acid supplied in polythene bottles is usually pure, but it is advisable to test a sample. A correction must be applied if there is any non-volatile residue after evaporation.

“Silica” as an Insoluble Residue

In many minerals, slags, and technical products, the residue left after treatment with acid is mainly silica. It is often permissible, *e.g.* in analyses made for technical purposes, to report the insoluble residue, without further examination, as

¹ Because of its action upon glass, hydrofluoric acid is kept in polythene bottles. The liquid, usually about 40 per cent. hydrofluoric acid, should be handled with the ordinary care taken with corrosive acids, and its evaporation must be carried out in a good draught, as its vapour is poisonous. It should be handled in polythene apparatus. See also p. 60.

“ silica ” or “ silica and insoluble silicates.” Typical examples of the determination of “ silica,” where “ silica ” means only the portion insoluble in acid, are described under Dolomite (p. 436) and Pyrites (p. 428). In these determinations some of the silica usually dissolves ; but, on the other hand, the residue is not entirely silica, and for many purposes the uncorrected results are sufficiently accurate.

When an accurate determination of the silica is required, the following modification is necessary :—The “ silica ” must be evaporated with hydrofluoric and sulphuric acids and the weight of the non-volatile residue ascertained (p. 389). This residue must then be fused with sodium carbonate, or fusion mixture, and added to the main solution. This must be evaporated to complete dryness, and the small amount of silica present separated in the manner already described (p. 389).

SILVER

The volumetric method for the determination of silver, described on pp. 194 and 197, is convenient and accurate.

Gravimetrically, silver is usually determined as chloride, but the gravimetric determination as silver bromide is recommended.

Traces of silver in lead can be determined by a method depending on the displacement of the former from solution by means of metallic copper (Evans, *Analyst*, 1926, 51, p. 79).

For a colorimetric method see Cave and Hume, *Anal. Chem.*, 1952, 24, 1503.

Forms in which Silver is precipitated

Silver Chloride.—Silver may be determined by this method in presence of all other metals. The silver is precipitated with dilute hydrochloric acid, carefully avoiding unnecessary excess. If a mercurous salt is present, it must be oxidised with concentrated nitric acid prior to the precipitation of the silver. If lead is present, the solution must be diluted so that it contains not more than 0.2 gram of the substance in 150 ml., and the hydrochloric acid must be added very slowly. Otherwise the procedure is identical with that adopted in determining chloride as silver chloride (p. 255).

Silver Bromide.—This method is preferable to the chloride method on account of the lower solubility of silver bromide.

The solution is acidified with nitric acid and potassium bromide added until precipitation is complete. The procedure is otherwise identical with the previous method. For the properties of silver bromide, see p. 326.

SODIUM

Sodium may be determined directly by precipitation as the triple salt, sodium zinc uranyl acetate. It is often determined together with potassium (see p. 383), but in cases in which sodium alone is present in combination with volatile acids, it may be determined conveniently as the sulphate, Na_2SO_4 .

Sodium may be determined by flame photometry (see p. 510).

Determination of Sodium as Sodium Zinc Uranyl Acetate

OUTLINE OF METHOD.—A small volume of the solution containing the sodium salt is stirred with ten times its volume of a zinc uranyl acetate reagent. The triple acetate precipitated is filtered off on a Gooch or sintered glass crucible, and after washing with alcohol and ether is dried and weighed as $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$.

Sodium Zinc Uranyl Acetate, $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$, is a yellow crystalline solid. It separates even from a N/500 solution of sodium chloride when this is treated with considerable excess of a reagent consisting of a concentrated solution of zinc and uranyl acetates saturated with the triple acetate. Though fairly soluble in water, the triple acetate only dissolves to the extent of 0.5 gram per litre at 22° in 95 per cent. alcohol. It is slightly more soluble in absolute alcohol. Its solubility in the reagent increases considerably as the temperature rises, so that the temperature of the mixture when filtered during a determination should be approximately the same as that at which the reagent is filtered to remove the triple acetate after saturation.

Since the molecular weight of the triple acetate is very large, the amount of sodium suitable for a determination should not exceed about 15 mg., and the volume of the solution containing the sodium salt must also be small (about 2 ml.) in order to precipitate the sodium as completely as possible. The amount of potassium present should not be greater than 15 mg. per ml. The ammonium ion does not interfere if present in reasonable amount, but lithium forms a triple salt less soluble than that of potassium. Barium, calcium, and magnesium do

not interfere, but phosphate and arsenate, if present, must first be removed by being allowed to stand in contact with zinc carbonate for at least six hours.

In preparing the reagent a pure sample of uranyl acetate must be used, as many commercial samples contain considerable amounts of sodium, resulting in a heavy precipitate of the triple acetate with consequent weakening of the reagent. To 175 ml. of water add 5.5 ml. of glacial acetic acid, and heat the mixture to about 80°. Add 20 grams of uranyl acetate (dihydrate) and 6 grams of zinc acetate (dihydrate). After stirring until the salts have dissolved, cool to room temperature and if no solid has separated add 1 to 2 ml. of N/10 sodium chloride. Allow the reagent to stand for not less than twenty-four hours, and filter just before use, noting the temperature.

Procedure.—If a 2 ml. pipette is available, prepare a solution of sodium chloride by weighing accurately about 1.5 gram of the ignited salt, dissolving it in water, and making it up to 100 ml. Measure out 2 ml. of this solution into a small beaker for each determination. Otherwise weigh out 0.03 gram of sodium chloride into a small beaker, and add 2 ml. of water. In either case add 20 ml. of the filtered reagent, stir the mixture for several minutes to prevent supersaturation and allow it to stand for not less than half an hour at a temperature as near as possible to that at which the reagent was filtered. Filter off the crystalline precipitate on a Gooch or No. 4 sintered glass crucible. Transfer the precipitate with small quantities of the reagent with the help of a rubber-tipped glass rod, and wash it in the crucible five times with 2 ml. portions of 95 per cent. alcohol, using a small wash-bottle or pipette, and finally with a few millilitres of ether. Dry at 40° to 50°, cool, and weigh. One gram of the triple acetate contains 14.95 mg. of sodium.

Note.—Since the solubility of the triple acetate in 95 per cent. alcohol is very small, it is only necessary to saturate the alcohol used for washing with the triple acetate if less than 4 mg. of sodium is being determined.

Determination of Sodium as Sodium Sulphate

Dissolve about 0.4 gram of sodium chloride in a little water in a small weighed dish, preferably of platinum. Add 10 ml. of normal sulphuric acid, and carefully evaporate the solution, first on a water-bath, and then by means of a very small flame,

until no further evolution of white fumes takes place. Now raise the temperature to the full heat of the Bunsen for a short while. Cool, and sprinkle a small quantity of solid ammonium carbonate over the salt to decompose any sodium bisulphate, and heat with the blowpipe for ten minutes. Cool in a desiccator, and weigh. Repeat the ignition until the weight is constant.

STRONTIUM

Forms in which Strontium is precipitated

Strontium Sulphate.—This is the best method for strontium, but barium, calcium, and lead must be absent.

Strontium Carbonate.—In the absence of other metals which form insoluble carbonates, strontium can also be satisfactorily determined by precipitation with ammonium carbonate. Strontium carbonate can be weighed as such, being less easily decomposed by heat than calcium carbonate.

Strontium Nitrate.—Strontium is precipitated in this form when it is necessary to determine it in the presence of calcium, strontium nitrate being insoluble in nitric acid of specific gravity greater than 1.460, and in anhydrous acetone.

Determination of Strontium as Sulphate

Procedure.—Weigh out accurately about 0.8 gram of crystalline strontium chloride, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, into a 400 ml. beaker, and dissolve it in 100 ml. of water. Add 15 ml. of dilute sulphuric acid, and 100 ml. of alcohol. Stir thoroughly, and allow the mixture to stand overnight. Filter off on paper, and wash with a mixture of alcohol and water (55 ml. of 95 per cent. alcohol and 45 ml. of water), until all the sulphuric acid has been removed. Incinerate the paper in a platinum or porcelain crucible apart from the precipitate, since strontium sulphate is rather easily reduced to sulphide. Treat the ash from the paper with 2 or 3 drops of a mixture consisting of 1 ml. of alcohol and 2 drops of concentrated sulphuric acid. Warm very gently until the excess of sulphuric acid has volatilised. Add the precipitate and ignite at the full heat of the Bunsen burner, taking care to avoid access of reducing gases to the crucible (see p. 236). Weigh as SrSO_4 .

If barium is present, this must first be separated as chromate as described on p. 322, but the precipitate, being contaminated

with strontium, must be dissolved in dilute hydrochloric acid, and the barium again precipitated as before. The combined filtrates, after the addition of 5 ml. of dilute hydrochloric acid, are evaporated to half their bulk, and the strontium is precipitated as carbonate by ammonium carbonate after neutralisation with ammonia. The precipitate is filtered off, dissolved in hydrochloric acid, and the strontium determined as sulphate as described above.

Determination of Strontium as Nitrate

Procedure.—Weigh out accurately about 0.2 gram of pure strontium chloride, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, and dissolve it in exactly 10 ml. of water in a small dry beaker. Add 26 ml. of pure fuming nitric acid (sp. gr. 1.520) drop by drop from a burette with continuous stirring. Allow to stand for three or four hours, and filter through a No. 4 sintered glass crucible. Transfer and wash the precipitate with nitric acid made by diluting the 1.520 sp. gr. acid with water in the proportion of 26 ml. of acid to 10 ml. of water. Dry at 130° , and weigh as $\text{Sr}(\text{NO}_3)_2$.

Separation from Calcium.—In using this method for the determination of strontium in the presence of calcium, it is important that the final concentration of the nitric acid during precipitation should not be greater than that given above, as calcium nitrate may be precipitated in more concentrated acid.

An alternative method for separating these metals depends on the fact that calcium nitrate is soluble in anhydrous acetone whereas strontium nitrate is almost insoluble. The mixed nitrates must be extracted for at least an hour under a reflux condenser in order to remove the calcium nitrate completely. The strontium nitrate remaining is then weighed and the calcium in the extract determined after precipitation as oxalate.

Prepare a mixture of the two nitrates by weighing accurately about 0.3 gram of Iceland spar and about 0.3 gram of strontium carbonate into a small covered beaker and adding about 6 ml. of dilute nitric acid. After dissolution of the carbonates remove the cover, rinse it into the beaker and evaporate on the hot plate at such a rate that the liquid does not quite boil. When solid begins to separate care must be taken to avoid any spurting. Finally, heat the beaker to about 170° in an air-oven or on a hot plate with the bulb of a thermometer against the outside

of the beaker and covered with a little asbestos fibre. Cool in a desiccator and leave until ready for the extraction. Weigh a No. 3 sintered glass crucible, previously heated to 170° , and support this as described on p. 357 for the extraction of lithium chloride. Add about 25 ml. of anhydrous acetone to the cold mixture of calcium and strontium nitrates in the beaker and stir with a glass rod. The residual solid easily becomes detached, and is transferred to the sintered glass crucible by means of a stream of acetone from a small wash-bottle. Another 25 ml. should be sufficient for this purpose. Attach the reflux condenser and carry out the extraction for about an hour and a half as described on p. 357, but the glass rod used in transferring the nitrates to the crucible need not be left in the latter. Dismantle the apparatus and heat the crucible to about 170° in the air-oven. Cool the crucible in a desiccator and determine the weight of the residual strontium nitrate.

If the extraction has been carried out for an hour and a half, further treatment should not be necessary. Comparison of the weight of the residual strontium nitrate with that equivalent to the weight of strontium carbonate taken will show whether this is the case.

Distil the acetone from the extract, and dissolve the calcium nitrate in water containing a little hydrochloric acid. Make up the solution to 100 ml. in a graduated flask, and filter through a dry filter, neglecting the first few millilitres. Precipitate calcium oxalate from 25 ml. portions, and titrate as described on p. 124. Compare the weight of the original Iceland spar with that of the calcium carbonate equivalent to the calcium found by titration.

Alternatively the total calcium may be precipitated as oxalate and weighed as the monohydrate as described on p. 262.

SULPHATE

A volumetric method for the determination of sulphate in ordinary concentrations is given on p. 202.

Sulphate is usually determined gravimetrically as barium sulphate. For details, see p. 260.

SULPHIDE

A volumetric method for the determination of hydrogen sulphide is described on p. 162. Many sulphides are readily

decomposed by dilute acids, and the volumetric method may therefore be adapted to their determination.

In order to determine sulphide gravimetrically, a weighed sample (or measured volume) is decomposed with hydrochloric acid in an apparatus similar to that shown in Fig. 36, p. 166. To prevent liberation of sulphur by atmospheric oxidation, the apparatus must be filled with carbon dioxide or hydrogen. The hydrogen sulphide is led into a solution of ammonia and hydrogen peroxide, and is thereby oxidised to sulphate. The sulphate is determined in the usual manner as barium sulphate.

The oxidation of the hydrogen sulphide may also be effected by absorbing the gas in sodium hydroxide solution, and then adding bromine.

Traces of hydrogen sulphide in gases may be determined by the method described on p. 498.

The determination of sulphur in mineral sulphides is described in connection with the analysis of Iron Pyrites (p. 428), Copper Pyrites (p. 430), and Zinc Blende (p. 432).

SULPHITE

A volumetric method for the determination of sulphite is described on p. 161.

Traces of sulphur dioxide in air or flue gases may be determined by the method described on p. 498.

TIN

Tin is a constituent of many alloys, such as solder, type metal, bearing (anti-friction) metal, bronze, etc. Apart from its occurrence in alloys, it is rarely met with in analysis except as cassiterite, which is mainly stannic oxide.

The determination of tin is best accomplished by volumetric methods, which are far more reliable than any gravimetric methods. The latter are usually troublesome and are often inaccurate, more especially when the determination involves the separation of the tin from antimony, arsenic, lead, and copper, with which it is commonly associated. The volumetric method described on p. 170 is applicable to tin alloys and ores containing also antimony, arsenic, lead, and copper.

A concise account of the most reliable and rapid methods for the determination of tin in its ores and alloys is given in Parry's *The Assay of Tin and Antimony*.

Forms in which Tin is precipitated

Stannic Acid.—Tin may be precipitated in this form either from a solution containing a stannic salt only, or by the disintegration of an alloy by nitric acid. The insoluble stannic acid is then ignited and weighed as stannic oxide. The oxide, however, retains appreciable amounts of the oxides of other constituents in the case of an alloy. If the amount of tin present in the alloy is less than 2 per cent., the error involved may usually be neglected; but if it exceeds 2 per cent. it is necessary to remove the tin, and determine the weight of the residual oxides by the method described below. An alternative procedure is given under the analysis of a fusible alloy on p. 422. Neither of these methods is applicable to alloys containing antimony, arsenic, phosphorus, or (in the case of the former method) bismuth.

Stannic Sulphide.—Tin is completely precipitated in this form by hydrogen sulphide in presence of hydrochloric acid the concentration of which is not higher than 2N. The precipitate may be oxidised by ignition in air and the stannic oxide weighed; or it may be dissolved in hydrochloric acid (with addition of potassium chlorate) and the tin in solution determined volumetrically.

Stannic sulphide is not precipitated from a solution containing 15 per cent. of hydrochloric acid (about 4N) or an excess of oxalic acid (contrast antimony sulphide, p. 319).

Determination of Tin as Stannic Oxide

A. In a solution of a Tin Salt.

Procedure.—Weigh out accurately about 0.2 gram of stannous chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, and dissolve it in a mixture of 15 ml. of water and 10 ml. of dilute nitric acid in a 500 ml. beaker. Heat to boiling to oxidise the tin to the stannic state, and cool. Add 1 ml. of methyl orange, and run in dilute ammonia from a burette until the pink tinge has disappeared. Add 20 grams of pure ammonium nitrate, stir to dissolve, dilute to 250 ml., and heat to boiling. Allow the precipitate

to settle, and filter. Wash with 2 per cent. ammonium nitrate solution, dry in a steam-oven, and ignite the precipitate in the filter in a porcelain crucible, and weigh as SnO_2 .

B. In an Alloy.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid, and the insoluble stannic oxide formed is filtered off, washed, dried, and ignited. After being weighed, the tin is volatilised by heating with ammonium iodide, and the weight of the residual impurities after reconversion to oxide deducted. Arsenic, antimony, bismuth, and phosphorus must be absent.

Procedure.—Weigh out accurately about 2 grams of a sample of bronze into a porcelain basin. Cover the basin, and add a mixture of 10 ml. of concentrated nitric acid and 3 ml. of water; warm on a steam-bath until the alloy is completely disintegrated. Rinse the cover-glass, and evaporate the solution on a water-bath until the residue is pasty. Add 5 ml. of concentrated nitric acid, and warm gently for several minutes. Add 30 ml. of water, and heat to boiling. Filter through paper, wash the precipitate with warm water containing nitric acid, and then with water alone. Dry the filter, and ignite it in a weighed porcelain crucible. Weigh after cooling. Now mix the residue intimately in the crucible with 15 times its weight of powdered ammonium iodide. Heat the crucible inside a larger one to a temperature¹ between 400° and 500° (just below dark red heat) until no more fumes are evolved. Cool, add 2 to 3 ml. of concentrated nitric acid, and carefully evaporate to dryness on a hot plate. Decompose the nitrates by heating with a very small flame, and ignite at a low red heat to constant weight. The difference between this and the original weight gives the weight of pure stannic oxide obtained from the bronze. A sample of the ammonium iodide used should be tested in case any non-volatile impurity should be present.

TITANIUM

At one time regarded as a comparatively rare element, titanium is now recognised as one of the most widely distributed, and is more abundant in actual amount in the earth's crust than many more familiar elements such as tin, lead, carbon, and sulphur. It is probably an invariable constituent of all

¹ If iron is present the temperature must not rise above 475° .

silicate rocks, although usually present to the extent of only 1 per cent. or less, but seldom merely as traces. It is also met with as an alloy in ferro-titanium, and is sometimes present in cast-iron and steel.

The colorimetric determination of traces of titanium is described on p. 306, and the use of a solution of titanous sulphate as a reducing agent in volumetric analysis has been described on pp. 176-179.

In the gravimetric determination of titanium it is often necessary to separate it from other elements with which it is associated. It is usually weighed as TiO_2 after precipitation in some other form which on ignition gives the oxide. Insoluble compounds of titanium, including the oxide, may be brought into solution by fusion with potassium pyrosulphate (p. 439), followed by extraction with dilute sulphuric acid.

Forms in which Titanium is precipitated

Titanium Hydroxide.—Is precipitated by ammonia, and the precipitate is ignited to TiO_2 and weighed in the same manner as is iron in its determination as Fe_2O_3 (p. 251). In rock analysis the titanium will be precipitated together with hydroxides and phosphates of iron, aluminium, and manganese. The mixed precipitate, which after ignition contains titanium as TiO_2 , is brought into solution after fusion with potassium pyrosulphate, and the titanium may be determined colorimetrically.

Titanium Oxinate, $\text{TiO}(\text{C}_9\text{H}_6\text{ON})_2$.—Titanium may be separated in this form under suitable conditions from alkali metals, alkaline earth metals, and magnesium.

Complex with Tannin and Phenazone.—By the use of these reagents titanium may be separated from the elements with which it is most commonly associated (iron, aluminium, and manganese), and also from silicon and phosphorus.

Determination of Titanium by precipitation with Tannin and Phenazone (Antipyrine)

OUTLINE OF METHOD.—The acidified titanium salt solution is precipitated by tannin and phenazone, and the precipitate is ignited and weighed as TiO_2 .

Procedure.—A quantity of the sample, containing not more than 0.04 gram of titanium, is brought into solution if necessary by fusion with potassium pyrosulphate. To the solution in a

600 ml. beaker add ammonia until just alkaline, then 10 ml. of concentrated sulphuric acid, and 100 ml. of 4 per cent. tannin solution. Dilute to 400 ml., and add a 20 per cent. solution of phenazone in water, while stirring, until all the titanium has been precipitated as an orange-red flocculent precipitate. This is ascertained by allowing the precipitate to settle, and adding more phenazone solution, when, if no titanium remains, a white precipitate is produced with the excess of tannin present. Heat to boiling while stirring, and allow to cool. Filter off on paper, with the aid of gentle suction (p. 44), using if necessary two filters as the precipitate is very bulky. Wash with a solution containing 3 ml. of concentrated sulphuric acid and 1 gram of phenazone in 100 ml. of water. Dry the precipitate, and ignite very carefully with the filter in a weighed dish, preferably of platinum, heating finally with a Méker burner until all the carbon is burned away. Weigh the residue of TiO_2 .

TUNGSTEN

Tungsten is usually determined by a gravimetric method. It is weighed in the form of its trioxide after precipitation as a compound which gives this oxide upon ignition.

Forms in which Tungsten is precipitated

Tungstic Acid.—Tungsten is precipitated in this form in the determination of tungsten in steel (p. 425). Tungstic acid can also be precipitated from alkali tungstate solutions obtained after fusion with alkali hydroxide or carbonate.

Benzidine Tungstate.—Tungsten is precipitated as benzidine tungstate by the addition of benzidine hydrochloride more completely than it is by evaporation with acid to form tungstic acid.

Mercurous Tungstate.—For this method phosphates, arsenates, chromates, molybdates, and vanadates must be absent.

Determination of Tungsten as Trioxide after precipitation as Benzidine Tungstate

OUTLINE OF METHOD.—Excess of benzidine hydrochloride solution is added to the tungstate solution in the presence of sulphuric acid, giving a mixture of benzidine tungstate and benzidine sulphate which is easier to filter off than the former alone. On ignition tungsten trioxide only is left.

Tungsten Trioxide, WO_3 , is a canary yellow solid, difficultly fusible, and not volatile at a cherry red heat.

Procedure.—Grind 1 gram of benzidine with 40 ml. of 1 per cent. hydrochloric acid, transfer it to a beaker, and wash out the mortar with another 10 ml. of 1 per cent. hydrochloric acid. Heat to dissolve the solid, and filter.

Weigh out accurately about 0.25 gram of sodium tungstate, dissolve in about 100 ml. of water, add 1 ml. of methyl orange, and make the solution just acid by the addition of decinormal sulphuric acid. Then add 10 ml. more of the acid, heat to boiling, and add 15 ml. of the benzidine hydrochloride solution. Stir for some minutes, allow the mixture to cool completely, and filter through ashless paper. Wash the precipitate with water containing about one-twenty-fifth of its volume of the benzidine reagent until the filtrate leaves no residue on evaporation. Ignite the moist precipitate with a Bunsen in a weighed porcelain crucible at the lowest temperature at which all organic matter and carbon can be burnt off. Finally ignite at at least 600° . Weigh as tungsten trioxide.

Determination of Tungsten as Trioxide after precipitation as Mercurous Tungstate

OUTLINE OF METHOD.—Excess of a solution of mercurous nitrate is added to the solution of the tungstate in absence of chloride ions. The precipitate of mercurous tungstate is filtered off, washed, and ignited to tungsten trioxide.

Weigh out accurately about 0.25 gram of sodium tungstate, dissolve it in about 50 ml. of water, and make the solution *just* acid to methyl orange by the addition of nitric acid. Boil the solution to remove carbon dioxide, cool, and add a solution of mercurous nitrate (p. 515) until, after the precipitate has settled, it is found that no further precipitation occurs. Then add 3 ml. in excess. Stir the mixture, allow it to stand for four hours, filter through paper, and wash with a dilute solution of mercurous nitrate (1 part of the reagent to 10 parts of water). Dry in a steam-oven, transfer to a weighed porcelain crucible, and ignite with a Méker burner *in a fume cupboard*. The ignition temperature must be 850° at most. Weigh the residual oxide (WO_3) after cooling.

VANADIUM

Vanadium is determined both by gravimetric and by volumetric methods, the latter being generally more suitable. Volumetric methods depend on the reduction of quinquevalent vanadium to the quadrivalent condition and subsequent oxidation to the quinquevalent (p. 131). In the gravimetric determination vanadium is weighed as the pentoxide, V_2O_5 , which, though easily fusible, does not volatilise on gentle ignition.

For the colorimetric determination of vanadium see, for example, Talvitie, *Anal. Chem.*, 1953, **25**, 604.

Forms in which Vanadium is precipitated

Mercurous Vanadate.—This method may be used for the determination of a vanadate after fusion with alkali. Phosphates, arsenates, chromates, molybdates, and tungstates must be absent.

Lead Vanadate.—The composition of this compound is not constant, and accurate results can only be obtained by the removal of the lead as sulphate or sulphide, evaporation of the filtrate, and ignition of the residue to vanadium pentoxide.

Determination of Vanadium as Oxide after precipitation as Mercurous Vanadate

OUTLINE OF METHOD.—Mercurous vanadate is precipitated from a solution of an alkali or ammonium vanadate by the addition of a solution of mercurous nitrate, ignited to oxide, and weighed.

Procedure.—Weigh out accurately about 0.2 gram of ammonium vanadate, and dissolve it in about 70 ml. of hot water. Cool, and add a solution of mercurous nitrate (p. 515) drop by drop from a burette until no further precipitate is produced, the precipitate being allowed to settle after each addition. Then add about 3 ml. in excess.

Boil the mixture, and, after the precipitate has settled, filter off on paper, and wash the precipitate with a very dilute solution of mercurous nitrate (1 part of the reagent to 10 parts of water). Dry the filter, ignite it *in a fume cupboard*, cool, and weigh the residue of vanadium pentoxide.

In the case of a vanadate obtained by fusion with sodium carbonate and potassium nitrate, the strongly alkaline solution must be almost neutralised with dilute nitric acid, excess being carefully avoided, since any nitrite formed during the fusion would liberate nitrous acid, with the subsequent reduction of vanadate to a vanadyl salt which is not precipitated by mercurous nitrate.

WATER

Two gravimetric methods, with many modifications of each, are used for the determination of water. A volumetric method has been mentioned on p. 185. The accuracy of the determination often depends on the choice of the appropriate method.

(1) **Indirect Method.**—A weighed sample is heated to a high temperature and the loss of weight is determined. This method is not always applicable.

(2) **Direct Method.**—A weighed sample is heated and the water evolved is collected and weighed. There are many modifications of the method of heating the substance and of collecting the water. The direct method is more generally applicable than the indirect method, but is somewhat more troublesome.

Indirect Determination of Water

As this is the easiest method, it is used whenever possible. It is inaccurate—

- (1) If anything except water is lost during the dehydration. This is particularly liable to occur with carbonates, organic substances, and ammonium compounds.
- (2) If the substance is readily oxidised. The method therefore gives inaccurate results if, for example, ferrous salts are present.

The first error can be avoided in some cases by dehydrating at a low temperature by means of a current of dry air or in a vacuum. The second error is avoided by dehydrating in an oxygen-free atmosphere or in a vacuum.

Three of the many modifications of the indirect method may be mentioned :—

(1) Gentle ignition until constant weight is attained. The procedure has already been described for the determination of water in magnesium sulphate heptahydrate (p. 248).

(2) Drying in a steam-oven or hot air-oven at constant temperature. Many hydrated salts can be dried at temperatures between 100° and 200° without further decomposition. There is no fixed temperature at which all hydrated salts will become anhydrous, and it is therefore necessary to ascertain for each substance the temperature, if any, at which the water can be expelled without further decomposition.

The substance is weighed in a wide, shallow weighing-bottle, and the open bottle is placed in the hot air-oven for one hour. The bottle is then removed and cooled in a desiccator. The stopper must be replaced before weighing, as re-absorption of moisture may occur. The procedure is repeated until the weight is constant.

(3) Most substances may be dried without decomposition in a vacuum desiccator containing sulphuric acid or fused calcium chloride. The substance should be weighed in a wide, shallow bottle or on a watch-glass. Dehydration may proceed so slowly at the ordinary temperature that it becomes complete only after many days; if the substance is heated *in vacuo*, dehydration takes place more rapidly and there is no risk of oxidation.

Direct Determination of Water in a Mineral

If the mineral on ignition loses only water and carbon dioxide, the following simple method (Brush and Penfield's) is convenient and accurate.

The mineral is heated in a hard-glass tube (about 20 cm.

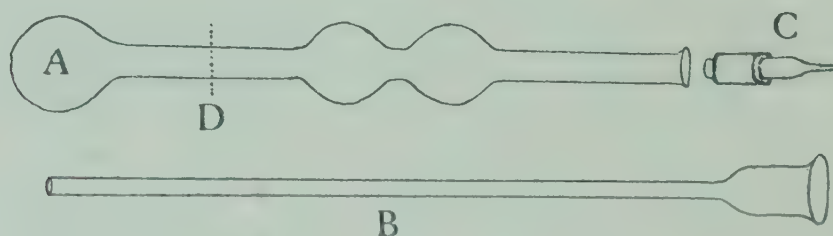


FIG. 73.

long and 5 mm. in diameter), which is enlarged into a bulb A (Fig. 73) at the closed end. One or more bulbs are provided near the middle of the tube in order to catch the water and prevent it running back and cracking the hot glass. A stopper C, for the open end of the tube, is made from a piece of tubing drawn out to a capillary and fitted with rubber tubing.

Even if apparently dry, these tubes must be thoroughly dried before use, by heating and blowing air through them by means of a narrow glass tube reaching to the bottom.

Procedure.—Weigh the empty bulb-tube. Introduce, by means of the tube B, from 0.5 to 1 gram of the substance, and weigh again. Insert the stopper C and clamp the tube in a horizontal position. Wrap strips of wet filter paper round the middle bulbs. Heat the bulb A, gently at first and then more strongly, with a Bunsen or a Méker burner, according to the temperature required to expel the water. It is advisable to protect the middle bulbs from the heat of the flame by means of a piece of asbestos board placed near the point D.

When the water has been completely expelled, draw off the heated end of the tube in a small blowpipe flame at the point D. Clean and dry the tube externally, cool it for half an hour, and weigh it (without the stopper). Remove the water by warming the tube and aspirating air through it by means of tube B. Weigh the tube again after cooling.

If the substance contains sulphur, fluorine, etc., it must be mixed with some substance such as calcium oxide, to prevent the volatilisation of these elements.

Exercise.—Determine the percentage of water in gypsum or in barium chloride, heating with a Bunsen flame only.

ZINC

The volumetric method for the determination of zinc (p. 199) is more expeditious than the gravimetric methods, and is capable of yielding excellent results. The method requires practice, however. Zinc may also be determined volumetrically after precipitation as oxinate (p. 409).

Zinc is always determined after removal of the metals precipitated by hydrogen sulphide in acid solution. Zinc sulphide is partially precipitated with the sulphides of the copper group unless the solution is very strongly acid, and, in order to effect a complete separation, it may be necessary to redissolve the copper group precipitate, after filtration, and to reprecipitate with hydrogen sulphide.

For methods for separating iron and zinc, see p. 352. Zinc may be determined volumetrically in metallurgical materials by

means of EDTA (see Kinnunen and Merikanto, *Chemist Analyst*, 1952, 41, 76).

Forms in which Zinc is precipitated

Basic Zinc Carbonate.—This method is applicable only when all metals other than sodium and potassium are absent. It is inaccurate in presence of ammonium salts, but these can be removed before precipitation. For details, see p. 258.

Zinc Ammonium Phosphate.—This method is available in presence of sodium, potassium, and ammonium salts only.

Zinc Sulphide.—Zinc may be separated from the calcium group by precipitation as sulphide, and in general analysis this is frequently the only available method. As, however, it is a matter of considerable difficulty to obtain zinc sulphide in a form suitable for filtration, it is preferable, when circumstances permit, to precipitate as basic carbonate or as phosphate.

A complete separation of zinc from iron, aluminium, manganese, cobalt, and nickel is obtained by precipitation as sulphide in presence of formic acid.

Zinc Oxinate.—By the use of this method zinc may also be determined volumetrically.

Metallic Zinc (Electrolytic).—See p. 275.

Determination of Zinc as Phosphate

OUTLINE OF METHOD.—The zinc is precipitated as zinc ammonium phosphate by means of ammonium phosphate in a very faintly acid solution. It is weighed either as $\text{Zn}(\text{NH}_4)\text{PO}_4$ after drying at 120° , or as $\text{Zn}_2\text{P}_2\text{O}_7$ after ignition.

Zinc Ammonium Phosphate is a white, crystalline powder, insoluble in water and in solutions of ammonium salts, but somewhat soluble in ammonia. It is readily soluble in mineral acids, but is almost insoluble in very dilute acetic acid. It may be dried without decomposition at temperatures not exceeding 140° ; heated above 300° , it is converted into zinc pyrophosphate, $\text{Zn}_2\text{P}_2\text{O}_7$.

Zinc Pyrophosphate is a white powder which may be heated to dull redness without decomposition. Flame gases and carbonaceous matter must be carefully excluded during the ignition, otherwise reduction and volatilisation will occur.

Procedure (in absence of sodium and potassium).—The zinc solution should be just acid, and its volume should be about 100 ml. Add 6 to 10 times the theoretical amount of diammonium hydrogen phosphate, which has been dissolved in water and made just alkaline to phenolphthalein with dilute ammonia, and 3 grams of ammonium acetate. Heat on the steam-bath for an hour; in that time the precipitate should be crystalline and should have settled completely. Filter off on a Gooch or sintered porcelain crucible, wash with hot water, dry at 110° to 120° , and weigh as $\text{Zn}(\text{NH}_4)\text{PO}_4$.

The method above is accurate, but if it is desired to weigh as pyrophosphate, the crucible must be placed inside a platinum or nickel crucible and ignited—at first gently, but finally to redness. Care must be taken to exclude flame gases during the ignition, since reduction (with volatilisation of the zinc) occurs readily.

Note.—The conditions mentioned above must be rigidly adhered to during the precipitation, or precipitation will be incomplete.

Modification if Alkalis are present.—If sodium or potassium salts are present, even in small amount, the precipitate obtained is a mixture of zinc ammonium phosphate and zinc potassium (or sodium) phosphate.

When these salts are present, add 20 grams of ammonium chloride to the solution, and precipitate as described above. When the precipitate has settled, decant through a Gooch crucible and wash three times with hot water by decantation, care being taken that as little as possible of the precipitate is washed into the crucible.

Dissolve the precipitate in the beaker in the minimum amount of dilute hydrochloric acid, add 10 grams of ammonium chloride, and repeat the process of neutralisation and precipitation. Filter off on the crucible used in the first operation, wash thoroughly, ignite, and weigh as $\text{Zn}_2\text{P}_2\text{O}_7$.

It is necessary in this case to ignite to pyrophosphate, as in presence of large amounts of ammonium salts the zinc ammonium phosphate is contaminated with ammonium salts which are not completely removed by washing.

If only sodium salts are present, a single precipitation in presence of a large amount of ammonium chloride is sufficient. The precipitate must be converted into pyrophosphate.

Determination of Zinc as Sulphide, after Precipitation in presence of Formic Acid

OUTLINE OF METHOD.—The zinc is precipitated as sulphide by hydrogen sulphide in presence of a small amount of formic acid. The sulphide is converted into oxide by ignition in air and the ZnO weighed; or it may be ignited in hydrogen and weighed as ZnS.

Zinc Sulphide, obtained by precipitation, is a hydrated, gelatinous substance. It is readily soluble in strong acids, insoluble in ammonia and in alkaline solutions generally, and almost insoluble in dilute solutions of acetic or formic acids. Whatever the conditions of precipitation, it is somewhat difficult to filter off. The best precipitate is obtained from a slightly acid solution containing ammonium sulphate; it is then collected fairly readily, but, if washed with water, becomes more gelatinous and chokes the filter paper. It can, however, be washed with dilute solutions of ammonium salts.

Zinc sulphide is quickly oxidised to zinc oxide on ignition in air, and is therefore usually converted into oxide for weighing; it can, however, be dried and obtained as anhydrous ZnS by gentle ignition with sulphur in an atmosphere of hydrogen, using a Rose crucible.

Zinc Oxide.—The properties of zinc oxide are described on p. 259.

Procedure.—To the zinc solution contained in a 400 ml. conical flask, add 1 ml. of methyl orange, and then run in carefully a dilute solution of sodium hydroxide until the last tinge of pink is discharged (avoid excess). Dilute 5 ml. of ordinary 95 per cent. formic acid to 100 ml., and add this to the zinc solution until a faint permanent pink colour is obtained, and then add an additional 5 ml. of the 5 per cent. formic acid, and 5 grams of ammonium sulphate.

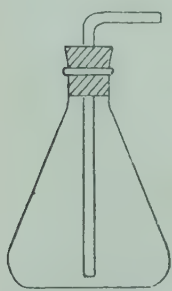


FIG. 74.

Dilute the solution to about 250 ml., heat to 80° , and saturate with hydrogen sulphide under slight pressure. Pressure a little above atmospheric is readily obtained with an ordinary Kipp apparatus if the flask is fitted with a rubber stopper (Fig. 74). The stopper is inserted firmly into place after the air in the flask has been displaced by hydrogen sulphide. When the solution is saturated and the precipitate has settled, the stopper is removed before the apparatus is disconnected elsewhere.

Decant, filter with slight suction, and wash with a saturated hydrogen sulphide solution containing 2 per cent. of ammonium acetate ; wash finally with hot water.

Dry the precipitate and filter paper thoroughly. Remove the precipitate as completely as possible from the filter paper, but do not rub off any paper fluff, since this would cause reduction and loss of zinc in the subsequent ignition.

If the sulphide is to be weighed, incinerate the paper in a Rose crucible before adding the precipitate. Add a little pure sulphur, ignite at a low red heat in a current of hydrogen (see p. 239) and weigh the ZnS .

If the sulphide is to be converted into oxide, incinerate the paper before adding the precipitate, and ignite in an open crucible with careful exclusion of flame gases. Weigh the ZnO .

Determination of Zinc as Oxinate

The use of oxine as a reagent is described under Aluminium (p. 316).

Procedure.—To the solution containing not more than 0.06 gram of zinc add about 2 ml. of dilute hydrochloric acid and 25 ml. of 2N ammonium acetate. The final volume of the solution should be about 60 ml. Warm to about 60° , and run in from a burette 1 ml. of the oxine solution, prepared as described on p. 317, for every 5 mg. of zinc present. After mixing, the solution should have a yellow colour showing the presence of excess of the reagent. Heat nearly to boiling, filter through a No. 3 sintered glass crucible, wash with hot water, dry at 130° , and weigh as $\text{Zn}(\text{C}_9\text{H}_6\text{ON})_2$.

Instead of the precipitate being dried and weighed, it may be dissolved in warm 4N hydrochloric acid and aliquot parts titrated with a bromate-bromide mixture as described under Aluminium (p. 317). The volume of oxinate solution taken for titration should not contain more than 0.015 gram of zinc. One ml. of decinormal bromate solution is equivalent to 0.817 mg. of zinc.

PART VI

EXAMPLES OF COMPLETE ANALYSIS INCLUDING SIMPLE ORES AND ALLOYS

WHEN a complete analysis of a substance is made, the sum of the ascertained percentages of the various constituents would be 100·0, if there were no experimental errors. In actual practice, this summation may be considered satisfactory if it lies between 99·5 and 100·5, and the results of a complete analysis ought always to be tested in this way. A satisfactory summation is, however, no proof that the analysis is accurate, since a positive error in the percentage of one constituent may balance a negative error in that of another. A summation may fall short of 100 because of mechanical losses (spilling of drops, spurting, etc.), or the slight solubility of precipitates, etc. ; or it may indicate that the substance contains other undetermined constituents. Errors from imperfect washing of precipitates, impurities in reagents, the action of solutions on glass, etc., may account for a summation exceeding 100.

Examples of typical analyses are given in the Appendix (p. 519). A full qualitative analysis of the material should be carried out before the quantitative work is begun, unless the constituents are already known.

The first step in the quantitative analysis of samples of materials containing a number of constituents is usually the preparation of a solution. If the substance is soluble in water it is only necessary to dissolve a suitable weight for the analysis. If insoluble in water it must be attacked by a suitable acid or mixture of acids, or in certain cases by fusion with sodium carbonate or fusion mixture, sodium peroxide or potassium pyrosulphate.

Most alloys should be attacked with nitric acid, the use of which avoids the risk of losing such volatile constituents as antimony, arsenic, mercury, phosphorus and sulphur, which would happen if hydrochloric acid was used alone. Alloys unattacked by nitric acid may require a mixture of nitric acid

and hydrochloric acid or sulphuric acid and sometimes addition of hydrofluoric acid is necessary. A mixture of sulphuric acid and hydrogen peroxide can often be used instead of nitric acid.

While some silicates may be brought into solution with hydrochloric acid, it is often necessary to fuse them first with sodium carbonate or fusion mixture and then separate the silica by evaporation of the melt with hydrochloric acid. If such a fusion is necessary the alkali metals must be determined in a separate sample by the Lawrence Smith method.

A solution of the original material having been obtained, the next step is the separation of the constituents present followed by the determination of these either in the form in which they are separated or after conversion into a more suitable compound for weighing, or by a volumetric process. The actual separation of the constituents is usually more difficult than their determination. To some extent the process of separation is similar to that employed in qualitative analysis, but these separations are often not sufficiently quantitative unless carried out with special precautions.

In quantitative analysis there are frequently alternative methods for the separation and determination of constituents of a complex substance. Which of these should be used may be decided by the available apparatus or by the presence of some other constituent which might interfere with a particular method of separation. For instance, in analysing alloys of copper it is possible to precipitate the copper as sulphide, as thiocyanate, or as metal by electrolysis, or by reduction with aluminium foil. If the apparatus is available it is best to separate the copper by electrolysis, but failing this the thiocyanate method is usually to be preferred. The separation as sulphide, though complete as far as the removal of copper is concerned, is less often used as it is troublesome to carry out, and zinc which is commonly present in copper alloys is liable to be post-precipitated on the copper sulphide, especially if filtration is delayed. Examples of these different methods for separating copper are given in the analyses which follow.

The determination of tin, lead, and antimony in alloys serves as another illustration of the use of alternative methods. If nitric acid is used for attacking the alloy, the tin and antimony are left as insoluble hydrated oxides which carry down small amounts of lead and certain other metals if these are present in

the alloy. In accurate work the tin and antimony oxides must be freed from these impurities. Alternatively, tin and lead may be determined in separate portions of the alloy after dissolution in hydrochloric acid, and antimony in a third portion after disintegration with concentrated sulphuric acid.

ANALYSIS OF COPPER—ALUMINIUM ALLOYS

Most of these alloys fall into two distinct classes: (*a*) aluminium bronzes in which copper is the main constituent, and (*b*) those, like duralumin, in which copper is less than about 12 per cent., the remainder of the alloy being chiefly aluminium. Although other elements are present in many of these alloys, the following analysis is concerned for the most part with the determination of copper and aluminium only. The classical method for the separation of copper as sulphide is described, although it could be more expeditiously determined as thiocyanate.

Outline of Method.—If the alloy belongs to class (*a*) it is dissolved in a mixture of sulphuric acid and hydrogen peroxide, while those in class (*b*) are brought into solution by a mixture of hydrochloric acid and hydrogen peroxide. After decomposition of the excess of hydrogen peroxide by boiling, the copper is precipitated by hydrogen sulphide, and the copper sulphide is removed by filtration and dissolved in nitric acid. The copper is either determined electrolytically or by titration with standard thiosulphate. Aluminium is precipitated in the filtrate by ammonia and weighed as aluminium oxide. If iron and manganese are present in the alloy, these may be determined volumetrically or colorimetrically after fusion of the impure aluminium oxide with potassium pyrosulphate, and an appropriate deduction made.

Procedure.—If the alloy belongs to class (*a*), weigh accurately about 0.8 gram of the finely divided turnings into a 250 ml. beaker. Cover this with a watch-glass and add about 10 ml. of water, 30 ml. of “20-volume” hydrogen peroxide and 5 ml. of concentrated sulphuric acid. Heat gently until all the metal has dissolved, adding more hydrogen peroxide if necessary. Boil the solution gently for about ten minutes to destroy the excess of hydrogen peroxide.

If the alloy belongs to class (*b*), weigh accurately about

4 grams of the finely divided turnings into a 600 ml. beaker. Cover with a watch-glass and add about 50 ml. of water and then 50 ml. of concentrated hydrochloric acid in small quantities at a time, avoiding a too vigorous reaction. In order to bring the copper into solution add about 60 ml. of "20-volume" hydrogen peroxide and heat gently. If after five minutes some copper is still undissolved, add a little more hydrogen peroxide. The excess of hydrogen peroxide is then destroyed by boiling.

If the amount of silicon in the alloy is believed to be more than a negligible quantity, it should be removed by evaporation in a porcelain dish on the water-bath in the case of the hydrochloric acid solution of the alloy. This method of rendering the silica insoluble, and its removal from the solution are described on p. 387. If sulphuric acid has been used in attacking the alloy the solution is evaporated by heating the beaker on the hot plate until thick white fumes are evolved. After complete cooling and dilution with about 100 ml. of water the beaker is heated until the copper and aluminium sulphates are dissolved. The solution is filtered and the paper and silica thoroughly washed.

Copper is now precipitated as sulphide in the filtrate from the silica, or in the original solution of the alloy if the silicon is present only in traces. Transfer the solution to a 300 ml. conical flask, dilute if necessary to about 150 ml., and heat the solution nearly to the boiling point. Pass a slow current of hydrogen sulphide through the hot solution until the precipitate is quite black and settles quickly, and the supernatant liquid is clear and colourless. The rate at which the hydrogen sulphide is absorbed is greatly increased if the gas-inlet tube is expanded to a bulb which rests on the mouth of the flask when the tube dips into the liquid. The precipitation takes at least half an hour.

In the meanwhile prepare some hydrogen sulphide solution by passing the gas into water contained in a special wash-bottle fitted for use with a valve (Fig. 17, p. 44).

When the precipitation is complete, remove the gas-delivery tube, and rinse it into the flask, rub off any adhering precipitate by means of a rubber-tipped glass rod, and rinse the tube again internally as well as externally, and also the rod. Decant the liquid through a 9-cm. filter, and with the help of the hydrogen sulphide solution transfer the precipitate at once to

the filter. Wash the precipitate and filter, especially the margin of the latter, with hydrogen sulphide solution until the washings are no longer acid to litmus paper. During the whole process of filtration and washing, the precipitate must be kept covered with the washing liquid as far as possible to prevent partial oxidation and consequent dissolution of the precipitate. Keep the filtrate and washings for the aluminium determination.

Make a hole in the bottom of the filter with a drawn-out glass rod, and wash the precipitate into a conical flask. Pour hot diluted nitric acid (1 of nitric acid with 2 of water) all round the top of the filter to dissolve the copper sulphide, and wash with water. Dry the filter, ignite it in a crucible, and set on one side. Boil the contents of the flask until brown fumes cease to be evolved. Cool, and filter from the sulphur into a 250 ml. standard flask. Wash the filter, dry, and ignite it in the same crucible. Cool, add 0.5 ml. of concentrated nitric acid and 1 ml. of water and carefully heat until the black residue has dissolved. Dilute, and filter through a small filter into the 250 ml. flask. Wash the crucible and filter into the flask, and make up to the mark. Determine the copper in 100 ml. of this solution by titration with standard thiosulphate as described on p. 159, taking care to remove nitrous acid before the titration. Alternatively, the copper may be determined electrolytically with a rotating electrode (see p. 272).

Aluminium.—Boil the filtrate from the copper sulphide precipitation to remove hydrogen sulphide, and in the case of a class (a) alloy of which about 0.8 gram was used, determine the aluminium in the whole of the filtrate by the method described on p. 254. In the case of a class (b) alloy, of which about 4 grams were used, boil to remove hydrogen sulphide, cool and make up to a litre in a graduated flask. Mix thoroughly and take 25 ml. of the solution for each determination.

If iron and manganese are present in the alloy, they will be precipitated along with the aluminium, and an appropriate deduction must be made from the weight of impure oxide. The determination of iron and manganese in the solution obtained after fusion of the precipitate with potassium pyrosulphate is described on p. 438. From the weights of iron and manganese found, calculate the corresponding weights of

Fe_2O_3 and Mn_3O_4 in the total weight of the impure oxide. If the iron content is too small for a volumetric determination it may be estimated colorimetrically as described on p. 290. In cases where the aluminium solution has been made up to a litre, the iron may be determined in a part of this solution, but because of the presence of chloride, the manganese is best determined in the aluminium oxide precipitate.

ANALYSIS OF A GERMAN SILVER

(Alloy of Copper, Nickel, Zinc, with traces of Iron)

OUTLINE OF METHOD.—The alloy is dissolved in nitric acid, and the solution is evaporated with sulphuric acid until all the nitric acid is expelled. The *copper* is precipitated and weighed as cuprous thiocyanate (precipitation with hydrogen sulphide tending to carry down a little zinc). *Iron* is removed by double precipitation with ammonia. *Nickel* is determined in the filtrate from the iron by means of dimethylglyoxime. *Zinc* is precipitated in the filtrate from the nickel as zinc ammonium phosphate.

Procedure.—Weigh accurately about 0.4 gram of the alloy, and place it in a small porcelain basin covered with a clock-glass. Add 2 ml. of water, and 5 ml. of concentrated nitric acid; warm gently until the alloy is dissolved, adding a little more nitric acid if necessary. Rinse the cover-glass, and evaporate to dryness on the water-bath. Cool, add 2 ml. of concentrated sulphuric acid, and heat carefully on a sand-bath until copious white fumes are evolved. Allow to cool; cautiously add 40 ml. of water, and stir to dissolve the sulphates.

Copper.—Add ammonia until the solution is only slightly acid, precipitate and weigh the copper as cuprous thiocyanate as described on p. 342.

Iron.—Evaporate the filtrate from the cuprous thiocyanate to about 30 ml., and to the hot solution add concentrated nitric acid *drop by drop* until no more brown fumes are evolved. (These fumes are poisonous.) This process not only decomposes the thiocyanate, but also oxidises the iron. Add ammonia in slight excess, and heat. Filter through a small paper, wash the ferric hydroxide with a little hot water, and set the filtrate and washings aside. Dissolve the precipitate on the filter with about 10 ml. of hot dilute hydrochloric acid, receiving the

solution in the beaker in which the precipitation of iron took place. Reprecipitate the ferric hydroxide with ammonia ; filter it off on the same paper, and wash thoroughly with a 2 per cent. solution of ammonium nitrate. The precipitate may either be ignited and weighed as Fe_2O_3 (p. 254) ; or, if too small for this, may be dissolved in dilute hydrochloric acid, and the solution made up to a known volume and the iron determined colorimetrically (pp. 290, 292, and 293).

Nickel.—Combine the two filtrates from the iron precipitations, make the solution only just acid with hydrochloric acid, and determine the nickel by means of dimethylglyoxime (p. 371).

Zinc.—To the filtrate from the nickel determination add 5 ml. of concentrated hydrochloric acid, and boil for fifteen to twenty minutes to remove alcohol and excess of dimethylglyoxime. Adjust the volume to about 100 ml. and determine the zinc as zinc ammonium phosphate (p. 406).

ANALYSIS OF SOLDER

Commercial solder consists essentially of lead and tin (from 30 to 60 per cent. of the latter), but it usually contains also from 1 to 3 per cent. of antimony. When such an alloy is disintegrated with nitric acid, the insoluble residue consists of stannic and antimonie acids, together with a small amount of lead oxide, the quantity of which may be diminished by using concentrated nitric acid for the disintegration. The analysis of solder by the first method described below is therefore inaccurate since the presence of antimony is ignored, but the method may be used for a pure lead-tin alloy without very serious error. The second method is capable of giving accurate results with any lead-tin-antimony alloy, such as type metal.

OUTLINE OF FIRST METHOD.—The alloy is disintegrated with nitric acid which dissolves the lead and converts the tin into insoluble stannic acid. The stannic acid is separated by filtration, ignited, and weighed as stannic oxide. The lead in solution is determined as chromate or sulphate.

Procedure.—Roll the alloy into a thin foil, or obtain filings by rubbing it on a clean, medium-cut file. Place a weighed

portion (about 0.3 gram) in a porcelain basin, add 5 ml. of concentrated nitric acid, and cover the basin with a clock-glass. Heat gently until the alloy is completely disintegrated. If this process is very slow, a few drops of water may be added. Remove and rinse the cover-glass, and evaporate to dryness on the steam-bath. Add 5 ml. of dilute nitric acid and 20 ml. of water, and heat until boiling. Filter. Wash the stannic oxide with hot water containing a little nitric acid, and then thoroughly with water alone.

Dry the stannic oxide in the steam-oven. Incinerate the filter paper, together with the stannic oxide, in a porcelain crucible at as low a temperature as possible. When all the carbon has been burnt off, allow the crucible to cool, and add several drops of concentrated nitric acid to oxidise any reduced oxide. Heat gently until dry, and then ignite with a Méker burner until of constant weight. In order to exclude flame gases during the ignition, it is advisable to support the crucible on an asbestos screen (p. 236).

The stannic oxide may contain antimony oxide. It always contains some lead oxide, but if the procedure has been carefully followed, the amount of occluded lead oxide will not usually exceed 1 milligram. If desired, the stannic and antimony oxides may be removed by volatilisation with ammonium iodide (p. 398), and the lead in the residue converted to lead nitrate and added to the filtrate.

Determine the lead (in the filtrate from the stannic oxide) as sulphate or as chromate (p. 354). If the chromate method is used, add about 10 grams of sodium acetate in order to replace the nitric acid by acetic acid.

OUTLINE OF SECOND METHOD.—One portion of the alloy is dissolved in hydrochloric acid and the solution is evaporated to dryness. The residue is extracted with alcohol and the *lead chloride*, which is insoluble in alcohol, is weighed. Another portion of the alloy is dissolved in hydrochloric acid (with careful exclusion of air) and the *tin* in solution is determined volumetrically by means of standard iodine. In a third portion the *antimony* is determined volumetrically by standard potassium permanganate or potassium bromate.

Lead.—In a small conical flask warm about 0.5 gram of the finely divided alloy on the steam-bath with 20 ml. of concentrated hydrochloric acid. If it dissolves very slowly, pass

chlorine gas¹ through the hot liquid until dissolution is complete. Transfer the solution to a basin and evaporate on the steam-bath almost to dryness. Add 20 ml. of absolute alcohol and stir well. Filter through a Gooch or sintered glass crucible, porosity 3, and wash the lead chloride with absolute alcohol. In presence of antimony, it is better to use absolute alcohol through which hydrochloric acid gas has been passed for a short time. Dry the PbCl_2 in the steam-oven, and weigh.

Tin.—Fit a 200 ml. flask with a rubber stopper and delivery-tube bent so that it can dip into a beaker when the flask is supported in a sloping position. Place 25 ml. of concentrated hydrochloric acid in the flask, together with about 1 gram of marble in order to displace the air by carbon dioxide. Introduce about 0.2 gram (accurately weighed) of the solder, and at once insert the stopper and delivery-tube. Warm the acid gently (but do not boil), the delivery-tube meanwhile dipping into water contained in a small beaker. (Care must be taken, by maintaining a steady flame, to prevent the water running back into the flask.) When the solder has completely dissolved, remove the beaker of water and substitute another beaker containing sodium carbonate solution. Allow the solution to cool. Cooling may be hastened by holding the flask under the tap—the delivery-tube remaining in the sodium carbonate solution during the process.

When the solution is cold, drop a small chip of marble into it, and add about 75 ml. of cold air-free water (water that has been recently boiled and rapidly cooled). Titrate the solution at once with decinormal iodine, using starch as indicator.

The iodine solution must be standardised by means of pure tin (0.15 gram), or with standard sodium arsenite (p. 158).

Antimony.—Disintegrate about 1 gram of the alloy by heating with 20 ml. of concentrated sulphuric acid as described on p. 129, and determine the antimony volumetrically with either standard potassium permanganate (p. 129), or standard potassium bromate (p. 180).

¹ The chlorine may be readily obtained by very gently warming a small quantity of potassium permanganate with concentrated hydrochloric acid in a small flask.

ANALYSIS OF BRASS

(Alloy of Copper and Zinc, with small quantities of Tin, Lead, and Iron)

OUTLINE OF METHOD.—In one portion of the alloy, dissolved in sulphuric acid and hydrogen peroxide, the *copper* is determined either volumetrically (p. 159), electrolytically (p. 272), or gravimetrically as cuprous thiocyanate. After removal of copper, the *iron* is determined gravimetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another (large) portion of the alloy is disintegrated with nitric acid. The *tin* is oxidised to stannic oxide which is weighed, and the *lead* in solution is separated and determined as lead sulphate.

Copper.—In a small covered porcelain basin dissolve about 0.3 gram of the alloy (in the form of fine turnings) by warming with a mixture of 20 ml. of 4N sulphuric acid and 15 ml. of "20-volume" hydrogen peroxide.¹ If necessary, more hydrogen peroxide may be added later. When dissolution is complete, rinse the cover-glass, and evaporate as far as possible on a water-bath to decompose the hydrogen peroxide. Dilute to about 80 ml. and allow to stand some hours. If any lead sulphate or stannic oxide has separated, filter through a small filter, and after washing with normal sulphuric acid, neglect the residue. Add ammonia to the solution until it is only slightly acid, and determine the copper as cuprous thiocyanate (p. 342).

Iron.—Determine the iron in the filtrate from the cuprous thiocyanate as described under the analysis of German Silver (p. 415).

Zinc.—Combine the two filtrates from the iron precipitations, and make the liquid slightly acid with dilute hydrochloric acid. Adjust the volume to about 100 ml. by evaporation or dilution, and determine the zinc as zinc ammonium phosphate (p. 406).

Tin and Lead.—Place 5 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 15 ml. of concentrated nitric acid and 5 ml. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is

¹ By the use of these reagents instead of nitric acid the evolution of acid fumes during the subsequent evaporation is avoided. Nitric acid, however, is preferable if much tin or nickel is present.

pasty. Add 5 ml. of concentrated nitric acid, stir, and warm gently for several minutes. Then add 50 ml. of water and heat until almost boiling. Filter through a small paper, wash with hot water containing a little nitric acid, and then with water alone. Dry, ignite, and weigh the stannic oxide (p. 417).

Transfer the filtrate to a porcelain basin, and add 8 ml. of concentrated sulphuric acid. Evaporate on the steam-bath as far as possible, and then on a sand-bath until copious fumes of sulphuric acid are evolved. Cool, add 100 ml. of water cautiously, and stir to dissolve the copper and zinc sulphates. Set aside for an hour. Filter through a Gooch or sintered glass crucible, wash with dilute (1 : 30 by volume) sulphuric acid, and then with alcohol. Dry, and weigh the lead sulphate (p. 354).

ANALYSIS OF A BRONZE

A bronze is an alloy consisting essentially of copper and tin, but usually containing also some zinc, together with traces of lead, nickel, and iron. Gun-metal is composed nominally of ninety parts of copper and ten parts of tin. English bronze coins contain about ninety-five parts of copper, four parts of tin and one part of zinc. The amount of lead in bronze coins rarely exceeds 0.1 per cent., but much larger proportions of lead are present in some varieties of bronze. Aluminium bronze usually consists of about ninety parts of copper and ten parts of aluminium, but may contain tin and other metals.

It is assumed that the alloy under analysis contains copper, tin, and zinc, with traces of iron and lead. The method described will therefore apply to most varieties of bronze, slight modifications being necessary when aluminium or nickel is present.

OUTLINE OF METHOD.—One portion of the alloy is disintegrated with nitric acid. The insoluble stannic acid is filtered and washed, dissolved in a mixture of concentrated sulphuric and hydrochloric acids, and the *tin* in solution determined volumetrically. In the filtrate from the stannic acid, the *lead* is determined as lead sulphate. Copper is then removed by electrolysis, or as cuprous thiocyanate, and the *iron* is determined gravimetrically or colorimetrically, after precipitation as ferric hydroxide. The *zinc* is determined as zinc ammonium phosphate.

Another portion of the alloy is dissolved in aqua regia and the *copper* in solution is determined volumetrically.

Tin.—Place 2 grams of the alloy in a porcelain basin provided with a cover-glass. Add a mixture of 10 ml. of concentrated nitric acid and 3 ml. of water, and warm on the steam-bath until the alloy is disintegrated. Rinse the cover-glass, and evaporate on the steam-bath until the residue is pasty. Add 5 ml. of concentrated nitric acid, and warm gently for several minutes. Then add 30 ml. of water, and heat until almost boiling. Filter through an untared Gooch crucible, and wash the stannic acid with warm water containing nitric acid, and then with water alone.

Transfer the stannic acid and the asbestos to a 400 ml. conical flask, using about 25 ml. of water. Add (cautiously) an equal volume of concentrated sulphuric acid, and boil for two minutes. Take care to avoid "bumping." Then add 50 ml. of concentrated hydrochloric acid and boil for two minutes. (The stannic acid dissolves, although the presence of the asbestos obscures this.) Reduce the stannic salt with antimony powder and determine the tin by titration with decinormal iodine (p. 170).

Lead.—In the filtrate from the stannic acid, determine the lead as lead sulphate. The procedure is given under Brass (p. 419).

Removal of Copper.—Electrolyse the solution (after the removal of tin and lead), using either stationary electrodes (p. 270) or a rotating anode (p. 272). The weight of copper deposited may serve for a determination of the copper, but the result will be slightly low as part of the copper is retained by the stannic acid. The copper may also be removed by precipitation as cuprous thiocyanate (see p. 342).

Iron and Zinc.—Evaporate the solution (after removal of tin, lead, and copper) to about 20 ml., and determine the iron and zinc as described under Brass (p. 419).

Copper.—Dissolve 0.6 gram of the alloy by warming with a mixture of 6 ml. of concentrated hydrochloric acid and 2 ml. of concentrated nitric acid in a 200 ml. flask. Boil the solution and destroy nitrous acid (p. 160). Dilute with a little water, add ammonia until a precipitate forms, and then acidify with acetic acid. (The stannic acid precipitated by the ammonia does not wholly redissolve in the acetic acid.) Cool the solution and dilute to 100 ml. in a standard flask. Determine the copper in 25 ml. volumetrically (p. 160).

ANALYSIS OF A FUSIBLE ALLOY

(*Alloy of Bismuth, Lead, Tin, and Cadmium*)

The best-known fusible alloys are Newton's alloy (two parts of bismuth, five parts of lead, and three parts of tin), Rose's alloy (two parts of bismuth, one part of lead, and one part of tin), and Wood's alloy (four parts of bismuth, two parts of lead, one part of tin, and one part of cadmium). The method described below is applicable to any of these alloys.

OUTLINE OF METHOD.—The alloy is disintegrated with nitric acid.

The insoluble residue of impure stannic oxide is washed, dried, ignited, and weighed; it is then fused with sodium carbonate and sulphur. The soluble sodium thiostannate is removed by extraction with water. The insoluble residue of lead and bismuth sulphides is dissolved in dilute nitric acid. The bismuth is determined as basic nitrate, the lead as sulphate, and the necessary corrections for the amounts thus found applied to the tin, lead, and bismuth.

The filtrate contains bismuth, lead, and cadmium, as nitrates. After separation of the bismuth as oxynitrate, the lead is determined as sulphate. The cadmium is determined either electrolytically or by precipitation as sulphide.

Place a weighed portion (about 0.6 gram) of the alloy in a covered porcelain basin, add slowly 6 ml. of concentrated nitric acid diluted with 4 ml. of water, and heat gently if necessary until the alloy is disintegrated. When the reaction is complete, add about 30 ml. of water, and boil gently for a few minutes. Filter, and wash the insoluble residue, at first with hot dilute nitric acid, and then thoroughly with hot water.

Analysis of the Insoluble Residue

Tin.—The insoluble residue consists of stannic oxide with traces of bismuth and lead oxides. Dry, ignite, and weigh the impure stannic oxide as described on p. 417. After weighing the oxide, transfer it to a small mortar, powder it, and mix it intimately with six times its weight of a mixture of equal parts of pure sulphur and anhydrous sodium carbonate. Heat the mixture in a *covered* crucible, gently at first and then with a full Bunsen flame for five minutes. Allow the crucible to cool before removing the lid. Place the crucible in a beaker and boil with 100 ml. of water. The tin dissolves as sodium thiostannate and the lead and bismuth remain as insoluble sulphides. Filter,

wash the residue, incinerate the filter, and repeat the fusion. (As a rule, a single fusion is insufficient to bring all the stannic oxide into solution.) Extract with water, filter through a tared Gooch or sintered glass crucible, and wash the insoluble residue of lead and bismuth sulphides. Then pour boiling dilute nitric acid through the filter until the residue has dissolved. (A trace of the lead sulphide may be converted into insoluble lead sulphate; in case this has happened, use the same crucible for the filtration of the lead sulphate at a later stage.) Evaporate almost to dryness, dilute to about 20 ml. and add *very dilute* ammonia until the solution is only slightly acid. Filter, wash the basic bismuth nitrate with dilute ammonium nitrate solution, and convert it into oxide as described on p. 325. Weigh the Bi_2O_3 . To the filtrate from the basic bismuth nitrate, add 1 ml. of concentrated sulphuric acid and evaporate until dense white fumes are evolved. Cool, add 30 ml. of water, and proceed with the determination of the lead as sulphate as described on p. 354.

Calculate the weight of PbO corresponding to the weight of PbSO_4 obtained. Subtract the weights of lead and bismuth oxides from that of the impure stannic oxide, in order to obtain the weight of pure stannic oxide.

Analysis of the Soluble Portion

Bismuth.—The bismuth may be separated as basic nitrate, as described on p. 325. The following modification of the procedure is preferable, as it avoids the large dilution.

Evaporate the filtrate and washings on the steam-bath until all the liquid has disappeared. Add 20 ml. of water, stir thoroughly, and again evaporate to dryness. Add about 100 ml. of dilute (2 grams per litre) ammonium nitrate solution, and keep the mixture for an hour, with occasional vigorous stirring, before filtering. Wash the bismuth oxynitrate with dilute ammonium nitrate solution. Convert the bismuth oxynitrate into oxide, as described on p. 325, and weigh as Bi_2O_3 . Add the weight of bismuth oxide found in the crude stannic oxide.

Lead.—To the filtrate from the bismuth oxynitrate, add 3 ml. of concentrated sulphuric acid, and evaporate until dense white fumes of sulphuric acid are evolved. Proceed as directed on p. 354, but wash carefully about eight times with dilute

(about normal) sulphuric acid before washing with alcohol; reject the alcohol washings. Weigh the PbSO_4 , and add the amount found in the analysis of the insoluble residue.

Cadmium.—Determine the cadmium in the filtrate either electrolytically, as described on p. 274, or by precipitation as sulphide and conversion into sulphate. (For details, see p. 327.)

ANALYSIS OF STEEL

Steel always contains a certain amount of carbon, manganese, phosphorus, silicon, and sulphur; and, for special purposes, varying amounts of other elements such as chromium, tungsten, molybdenum, vanadium, nickel, and cobalt. The estimation of certain of these constituents is described elsewhere; manganese, p. 127, phosphorus, p. 112, chromium, p. 130.

Carbon.—The total carbon in steel is determined accurately by combustion of the metal in oxygen in a silica tube at a temperature of 1000° . The gases resulting from the combustion are passed over hot platinised asbestos, and then through "chromic acid mixture" to absorb oxides of sulphur. The carbon dioxide is taken up, after being dried, by passing through weighed soda-lime or potash tubes. (For details of procedure, see Scott's *Standard Methods of Chemical Analysis*, or other comprehensive work.)

Silicon and Sulphur in Steel

OUTLINE OF METHOD.—The steel is dissolved in nitric acid containing a little hydrochloric acid and potassium chlorate, whereby the silicon is converted into silica, which is ignited and weighed as such. The sulphur is converted into sulphate, which is determined as barium sulphate.

Procedure.—Weigh accurately about 5 grams of the steel into a porcelain dish of about 15 cm. diameter, and add 1 gram of potassium chlorate. The latter assists in the oxidation and fixation of the sulphur as sulphate. Cover the dish with a clock-glass, add 50 ml. of concentrated nitric acid, and then not more than 3 ml. of concentrated hydrochloric acid. Warm the dish carefully *in a fume cupboard*, and stop heating as soon as the reaction begins. When the reaction has moderated, heat the dish on a steam-bath. If there is any metal undissolved after heating the covered dish for half an hour add another

3 ml. of concentrated hydrochloric acid, and continue the heating. When all the metal has dissolved, add 20 ml. of concentrated hydrochloric acid, and evaporate as far as possible on the steam-bath after rinsing and removing the clock-glass. Cool, add 50 ml. of concentrated hydrochloric acid, and again evaporate as far as possible to complete the removal of nitric acid. Towards the end of the evaporation stir continuously, and in order to dehydrate the silica place the dish in an air-oven at 110° for one hour. Throughout the whole process contamination by sulphur dioxide from burning gas must be carefully avoided. Cool, and moisten the residue in the dish with 5 ml. of concentrated hydrochloric acid. After five minutes add 30 ml. of hot water, heat to dissolve the iron salts, and filter. Transfer all the residue from the dish to the filter, using a rubber-tipped¹ rod, by means of small quantities of 1 : 1 hydrochloric acid. Wash the filter with hot water until free from chloride. Keep the filtrate and washings for the sulphate determination. Partially dry the filter, ignite in a platinum crucible, and weigh the residue. The impure silica is then treated with hydrofluoric acid and sulphuric acid as described on p. 389.

Pour the cold filtrate and washings into a litre measuring flask containing 90 ml. of concentrated ammonia and 200 ml. of water, shaking the flask continuously during the addition. Make up to the mark, mix thoroughly, and allow the ferric hydroxide to settle. Siphon off about 600 ml. of the supernatant liquid, and filter through a dry filter into a 500 ml. flask, rejecting the first few millilitres of the filtrate. Evaporate the measured filtrate with the rinsings of the flask, to about 200 ml. on a steam-bath. Acidify the solution with dilute hydrochloric acid, and precipitate the sulphate in the boiling liquid with barium chloride in the usual manner.

Tungsten in Steel

OUTLINE OF METHOD.—The steel is dissolved in hydrochloric acid, the solution oxidised with nitric acid, and the tungstic acid formed is filtered off and weighed as tungstic oxide. This method is suitable for steels containing over 0.5 per cent. of tungsten.

Procedure.—Dissolve 2 grams of the sample in 40 ml. of concentrated hydrochloric acid in a 400 ml. beaker of tall form.

¹ Black rubber must be used, as red rubber contains sulphides.

Dissolution of the sample usually takes place slowly, and necessitates prolonged digestion just below the boiling-point. When the sample has been decomposed, heat to boiling, and carefully oxidise with concentrated nitric acid, avoiding excess.¹ Insoluble tungstic acid forms. Evaporate to a paste on a water-bath, allowing no portion of the residue to become dry.

To the residue add 60 ml. of 20 per cent. hydrochloric acid, boil for two minutes, and allow to stand for at least an hour. Filter off tungstic acid on a paper-pulp filter, and wash with hot 5 per cent. hydrochloric acid until free from iron. Any tungstic oxide which sticks obstinately to the beaker can be removed by wiping with a piece of filter paper soaked in ammonia solution. The paper is ignited with the precipitate.

Transfer the filter and precipitate to a platinum crucible, and ignite at a temperature not exceeding 850° , *i.e.* at a cherry-red heat. Cool, and treat the precipitate with hydrofluoric acid, together with a drop of sulphuric acid, evaporating carefully to dryness to remove silica, and avoiding any loss by spurting. Ignite to constant weight at a temperature not exceeding 850° .

The ignited tungstic oxide is usually contaminated with iron oxide, and with titania (if titanium is present in the steel). To correct for these, fuse with 5 grams of sodium carbonate, and extract the fused mass with water. Filter through a Whatman's No. 40 9-cm. filter, wash well with hot water, dry, and ignite the insoluble residue in the platinum crucible previously used. Cool, and weigh. This weight deducted from that of the previous residue, gives the weight of tungstic oxide, WO_3 , formed. From this calculate the percentage of tungsten in the steel.

Molybdenum in Steel

Dissolve 2 grams of sample (4 grams if the steel contains less than 0.5 per cent. molybdenum) in 20 ml. of concentrated hydrochloric acid in a 400 ml. beaker. Oxidise with the minimum of concentrated nitric acid, and evaporate to a syrup. Cool, redissolve in 25 ml. of N hydrochloric acid, and if tungsten is present digest to precipitate it as tungstic acid. Concentrate to

¹ To oxidise iron from the ferrous to the ferric state by means of concentrated nitric acid, add this *drop by drop* to the boiling solution until no further change in colour can be observed.

small bulk, dilute to 50 ml. with hot 0.5N hydrochloric acid, boil, and filter through a paper-pulp pad. Wash with 50 ml. of hot 0.5N hydrochloric acid. Cool the filtrate to less than 10°, add 2 ml. of saturated ferrous sulphate solution, and precipitate the molybdenum with α -benzoinoxime as described on p. 370.

Nickel in Steel

OUTLINE OF METHOD.—The steel is dissolved in hydrochloric acid, and after oxidation of the iron to the ferric state, the nickel is precipitated by dimethylglyoxime in presence of citric acid, which prevents precipitation of the iron when the solution is subsequently neutralised.

Procedure.—Dissolve 1 gram of the steel in 15 ml. of concentrated hydrochloric acid and 10 ml. of water in a 350 ml. beaker. To the boiling solution add concentrated nitric acid drop by drop until no further change in colour takes place. Dilute to 200 ml. Add 4 grams of citric acid dissolved in water, and then dilute ammonia until the solution is neutral to litmus paper. Add 2 grams of sodium acetate, dilute to 100 ml., heat nearly to boiling and add a slight excess of a 1 per cent. alcoholic solution of dimethylglyoxime. (Approximately 6 ml. of a 1 per cent. solution of dimethylglyoxime should be added for each 1 per cent. of nickel present.)

After allowing to stand for an hour or two (but not overnight) filter off on a Gooch or sintered glass crucible. Wash thoroughly with hot water, dry at 120° for an hour, and weigh.

Chromium and Vanadium in Steel

Weigh accurately about 2 grams of sample and transfer it to a 600 ml. beaker. Dissolve the sample in 60 ml. of dilute sulphuric acid, and oxidise with the minimum of concentrated nitric acid. Boil to expel oxides of nitrogen. Add 5 ml. of phosphoric acid, dilute to 300 ml., add a boiling rod (p. 20), and boil. Add 2 ml. of 1 per cent. silver nitrate solution and 20 ml. of a freshly prepared 10 per cent. ammonium persulphate solution, and boil for 10 minutes. Discharge the permanganate colour by adding 5 ml. of dilute hydrochloric acid and boiling for 10 minutes. Cool the solution, and titrate with decinormal ferrous ammonium sulphate solution until the yellow colour is discharged. Add an excess (say 5 to 10 ml.) of ferrous ammonium sulphate, and back-titrate the excess with decinormal permanganate until a pink colour is obtained that is

permanent for at least one minute. The ferrous ammonium sulphate used corresponds to the chromium in the steel.

Now add about 10 ml. of decinormal ferrous ammonium sulphate to reduce the vanadium to the quadrivalent state. Add 5 ml. of freshly prepared 15 per cent. ammonium persulphate solution and stir for one minute to oxidise the excess of ferrous salt. Titrate the vanadium with decinormal permanganate until a pink colour persisting for one minute is obtained. The volume of permanganate used corresponds to the vanadium in the sample.

ANALYSIS OF IRON PYRITES

Iron pyrites (pyrite) consists essentially of sulphide of iron, FeS_2 , and in a good specimen the amount of other elements is very small. In many specimens, however, the iron is partially replaced by copper, and traces of arsenic, cobalt, and nickel are often present. Most specimens contain also a certain amount of "gangue"—consisting of enclosed or adhering particles of sand or other siliceous matter.

The analysis of iron pyrites therefore involves, as a rule, the determination of "gangue," copper, iron, and sulphur. It is sometimes necessary to determine also traces of arsenic, nickel, and cobalt, and the method described below must then be modified to include the determination of these elements.

Iron pyrites may be analysed by the method described on p. 430 for copper pyrites, but the following method is probably preferable.

OUTLINE OF METHOD.—The finely divided mineral is oxidised by means of sodium chlorate and hydrochloric acid. The *insoluble residue* is filtered off, ignited, and weighed. The *sulphur*, which has been completely oxidised to sulphate, is determined as follows:—The iron is precipitated by addition of ammonia, and, without filtration, the sulphate is precipitated as barium sulphate. The solution is then acidified with hydrochloric acid, in order to redissolve the ferric hydroxide, and the barium sulphate is collected and weighed.

The *copper* is precipitated from the filtrate as sulphide, and the *iron* is then determined either volumetrically or by precipitation as hydroxide.

Decomposition of the Pyrites.—Place about 0.3 gram of the *finely powdered* pyrites in a *dry*, 200 ml. conical flask, mix

with 2 grams of powdered sodium chlorate, moisten with 3 ml. of water, and cool the flask and contents in ice. Add 20 ml. of concentrated hydrochloric acid, previously cooled in ice, and keep the flask in the ice for twenty to thirty minutes, with occasional *gentle* shaking. Remove the flask from the ice, so that the temperature will rise slowly. After about thirty minutes, warm the flask momentarily on the steam-bath, repeating this at intervals with gentle shaking, until the pyrites has entirely disappeared. The decomposition should proceed without the separation of sulphur, the oxidation of which, if it is in the form of lumps or liquid globules, is exceedingly tedious.

Transfer the solution, together with any insoluble gangue, to a porcelain basin, and evaporate to dryness on the steam-bath. Cover the dry residue with 5 ml. of concentrated hydrochloric acid, and, after five minutes, warm and add about 30 ml. of water. Filter into a 400 ml. beaker, and wash the residue with hot, dilute hydrochloric acid and then thoroughly with hot water. Incinerate the filter, ignite the residue strongly, and weigh. The residue consists, as a rule, of silica or insoluble silicates, and may usually be reported as "insoluble residue" or "gangue"; if, however, an analysis of it is required, proceed as directed on p. 389.

Sulphur.—Dilute the solution to about 200 ml. with cold water, and add ammonia in excess to the cold solution to precipitate the iron. Heat the solution until it boils, and precipitate the sulphate with a boiling solution of barium chloride, as described on p. 261. In order to estimate the quantity of reagent required, assume that the mineral is pure pyrites, and use 5 per cent. more than the calculated amount, dissolved in 25 ml. of water.

Add dilute hydrochloric acid to the mixture in which the barium sulphate and ferric hydroxide are suspended, and, with frequent stirring, make sure that the latter has completely dissolved. (Avoid unnecessary excess of acid.) Cover the beaker and set it aside for at least six hours. The barium sulphate should appear perfectly white. Filter, wash, and weigh the barium sulphate.

Note.—The temporary removal of the iron from solution as ferric hydroxide is necessary in order to obtain the barium sulphate free from occluded ferric salts (see p. 260).

An ion-exchange method of eliminating the interference of iron is given on p. 505.

Copper.—In the filtrate from the barium sulphate, precipitate the copper as sulphide, dissolve and titrate as described on p. 413.

Iron.—After removal of the copper, determine the iron either (a) volumetrically, or (b) by precipitation as hydroxide.

(a) Ascertain that the iron is present entirely as *ferrous* chloride; if not, saturate the solution again with hydrogen sulphide. Expel the hydrogen sulphide by passing a current of carbon dioxide through the boiling solution, and cool. Titrate the solution with standard potassium dichromate, using diphenylamine sulphonate as indicator (p. 144).

(b) Evaporate the solution in an open basin to expel hydrogen sulphide, oxidise with nitric acid, and proceed as described on p. 252.

ANALYSIS OF COPPER PYRITES

Copper pyrites (chalcopyrite) consists essentially of a copper-iron sulphide, CuFeS_2 , and in a good specimen of the mineral the amount of other elements is negligibly small. Many specimens contain traces of silver, and “gangue” is usually present.

The analysis of copper pyrites therefore presents a problem very similar to that of iron pyrites. The same methods are applicable to both, and copper pyrites may be analysed by the method described on p. 428, or, preferably, by the method described below.

OUTLINE OF METHOD.—In one portion of the mineral, the *sulphur* is oxidised by heating with sodium peroxide and sodium carbonate. The sulphate is then determined as barium sulphate.

Another portion of the mineral is decomposed with dilute nitric and sulphuric acids. The *insoluble residue* of silica, etc., is separated by filtration, ignited, and weighed. The *copper* in the solution is precipitated by means of aluminium and is collected on a Gooch or sintered glass filter, washed, dried, and weighed. The *iron* in the filtrate is determined volumetrically.

Determination of Sulphur

In a spun-iron crucible of about 30 ml. capacity mix 2 grams of dry sodium carbonate with 5 grams of sodium peroxide.

Add a weighed quantity (about 0.3 gram) of the finely powdered pyrites and carefully mix the contents of the crucible by stirring gently with a nickel spatula or a glass rod. Place the crucible in a hole of appropriate size cut in asbestos board (Fig. 41, p. 236); heat very gently for about ten minutes, and then fuse the contents of the crucible by heating more strongly, but not above dull redness. Lift the asbestos board by opposite corners and rotate the crucible occasionally so as to rinse down the sides with the molten mixture.

Remove the flame, and, as soon as the contents of the crucible become solid, place the crucible upright in a 500 ml. beaker containing about 30 ml. of water. Cover the beaker and upset the crucible with a glass rod. Warm gently to dissolve sodium salts, and then remove the crucible and rinse it into the beaker. Add (cautiously) 8 ml. of concentrated hydrochloric acid to decompose some of the alkali hydroxide and carbonate. Filter through paper pulp (p. 45) and wash the precipitate thoroughly with hot water. Transfer the solution to a 500 ml. beaker, neutralise (approximately) by adding concentrated hydrochloric acid, and then add 1 ml. of acid in excess. Dilute the solution to about 250 ml., heat until boiling, and precipitate the sulphate with a boiling solution of barium chloride in slight excess (p. 261). Set aside for at least six hours. Filter off (a Gooch or sintered porcelain crucible may be used), wash, and ignite the barium sulphate.

Determination of Copper and Iron

Place a weighed portion (about 0.4 gram) of the *finely powdered* pyrites in a porcelain basin or casserole provided with a cover-glass. Add 20 ml. of water, 5 ml. of concentrated nitric acid, and 5 ml. of concentrated sulphuric acid. Warm very cautiously, adjusting the heating so that there is a vigorous, but not turbulent, evolution of brown fumes. If this operation is properly conducted, there will be no residue of sulphur after about ten minutes' treatment; if any sulphur remains, continue to boil gently with occasional addition of a few drops of concentrated nitric acid. (If the sulphur collects into a single large bead, it may be removed from the solution by means of a glass rod, transferred to a crucible, dried, ignited, and any residue dissolved in nitric acid and returned to the main solution.)

When all the sulphur is oxidised, add a further 5 ml. of concentrated sulphuric acid, and evaporate on a sand-bath until copious white fumes of sulphuric acid are evolved; cool, and dilute the solution to about 40 ml. Heat the solution, and keep it hot until any anhydrous ferric sulphate has dissolved. Filter, wash with cold and then with hot water. Ignite and weigh the insoluble residue.

Copper.—Cut some sheet aluminium into pieces about 2 by 4 cm., and bend each piece at right angles across the middle. Place four of the pieces in the *hot* pyrites solution, cover the beaker, and heat gently on a hot-plate until the solution is colourless (about one hour). Cool the solution. Remove the aluminium with a glass rod and rinse the pieces carefully with a jet of water.¹ Collect the precipitated copper in a Gooch or sintered glass crucible, wash thoroughly with cold water and three times with acetone (reject the acetone washings), and dry in a steam-oven for twenty minutes. Cool, and weigh.

Iron.—Titrate the filtrate (without delay) with decinormal permanganate.

Note.—If the aluminium contains a trace of iron—which is very probable—a correction for this impurity is necessary, and the above procedure must be modified as follows:—(1) Weigh (to the nearest centigram) the aluminium sheet before and after using it to precipitate the copper. (2) In another beaker mix 80 ml. of water and 10 ml. of concentrated sulphuric acid; add a similar quantity of aluminium (four pieces), and warm on the hot-plate beside the pyrites solution. Cool, remove the aluminium, dry and weigh it. Titrate the solution with decinormal permanganate. (3) From the data obtained in (1) and (2) calculate the correction to be applied to the titration of the iron.

ANALYSIS OF ZINC BLENDE

Zinc blende consists essentially of zinc sulphide, but usually contains also traces of carbonate, cadmium, copper, lead, iron,

¹ Traces of copper may remain unprecipitated. If great accuracy is required, a solution of hydrogen sulphide should be added before filtering off the copper, and also used for washing the precipitate. In this case the copper and copper sulphide are dissolved in nitric acid, and a known fraction of the solution titrated with standard thiosulphate (p. 414).

and manganese. With most samples there is associated a certain amount of adhering siliceous matter.

OUTLINE OF METHOD.—One portion of the blende is decomposed with hydrochloric acid, and the *insoluble residue* is separated. *Lead* is determined in the filtrate as sulphate. After removal of lead, the *copper* is precipitated by means of hydrogen sulphide from a strongly acid solution; the *cadmium* is then precipitated in a similar manner from a slightly acid solution. After removal of the copper and cadmium, the *iron* is precipitated by means of “cupferron,” and the *manganese* is then separated as dioxide. In the filtrate, the *zinc* is determined as zinc ammonium phosphate, or volumetrically.

Sulphide and *carbonate* are determined in separate portions of the mineral.

One of the difficulties in this analysis is the separation of cadmium and zinc. The procedure given here is suitable for a zinc blende containing only a small quantity of cadmium.

Separation into Soluble and Insoluble Portions.—Introduce a weighed portion (1 to 1.5 gram) of the finely powdered zinc blende into a conical flask, and moisten the powder with water. Add about 20 ml. of concentrated hydrochloric acid, and close the flask loosely with a small funnel or glass bulb. Warm on the steam-bath until there is no further action, and then add from time to time a few drops of concentrated nitric acid. When the residue is white and when any sulphur has been brought into solution, add a further 10 ml. of concentrated hydrochloric acid, and boil for five minutes. Filter the *hot* solution through a small filter paper and wash with a boiling solution of hydrochloric acid (1 : 1 water and concentrated acid) in order to dissolve any lead sulphate. Wash the residue with hot water, and ignite it. Weigh, and report the result as “insoluble residue.”

Lead.—Evaporate the solution to about 10 ml., cool, add 3 ml. of concentrated sulphuric acid, and evaporate on a gently heated sand-bath until dense fumes of sulphuric acid are evolved. Cool, dilute to about 100 ml., and collect the precipitate of lead sulphate as described on p. 354. The precipitate must be thoroughly washed with dilute (normal) sulphuric acid before being washed with alcohol. (Reject alcohol washings.)

Copper.—Evaporate the filtrate and washings from the lead sulphate until they begin to evolve fumes of sulphuric acid. Cool, add 20 ml. of water and 20 ml. of concentrated hydrochloric acid, and saturate the solution with hydrogen sulphide.

Filter, and wash with a mixture of equal volumes of concentrated hydrochloric acid and saturated hydrogen sulphide solution, observing the precautions against oxidation mentioned on p. 414. Dissolve the cupric sulphide in nitric acid, and titrate a known fraction of the solution with standard thio-sulphate (p. 159).

Cadmium.—Evaporate the filtrate until fumes of sulphuric acid appear. Cool, add 5 ml. of concentrated hydrochloric acid, and transfer the solution to a conical flask, using hydrogen sulphide solution to rinse the basin. Then add slowly, with constant stirring, hydrogen sulphide solution until the volume is increased to about 150 ml. Saturate the solution with hydrogen sulphide, collect the cadmium sulphide, and convert it into sulphate as described on p. 327.

Iron.—Evaporate the filtrate from the cadmium sulphide to about 50 ml. Transfer to a beaker, add 1 ml. of concentrated nitric acid, boil to oxidise ferrous salt, and dilute to 100 ml. Determine the iron by the “cupferron” method (p. 350), or by a double precipitation with ammonia as described on p. 415, adding in this case 2 grams of ammonium chloride before each precipitation.

Manganese.—Boil the filtrate from the iron precipitation to destroy excess cupferron, or acidify it with sulphuric acid if the iron was precipitated with ammonia. Add 2 grams of ammonium persulphate dissolved in 50 ml. of water and bring quickly to the boil. Add ammonia until the solution is faintly alkaline. Boil for two minutes, filter at once without cooling, and wash the precipitate of hydrated manganese dioxide thoroughly with hot water. Dissolve the precipitate in hot concentrated hydrochloric acid containing a little sulphurous acid. Add 1 ml. of sulphuric acid, evaporate until the hydrochloric acid has been expelled, cool, dilute, and reprecipitate as before. Determine the manganese colorimetrically (p. 302).

Zinc.—After removal of manganese, determine the zinc as zinc ammonium phosphate (p. 406) or volumetrically (p. 199).

Sulphur.—Place a weighed portion (about 0.4 gram) of the *finely powdered* zinc blende in a 150 ml. conical flask. Add 20 ml. of a mixture of three parts concentrated nitric acid and one part concentrated hydrochloric acid, and immediately cool under the tap. After a few minutes, add two or three drops of bromine and warm very gently on the steam-bath until all the

sulphur has been oxidised. Boil for five minutes, and then transfer to a porcelain basin, using concentrated hydrochloric acid to rinse the flask. Evaporate to dryness, add 5 ml. of concentrated hydrochloric acid, and again evaporate to dryness. To the residue add 30 ml. of water and 10 ml. of concentrated hydrochloric acid, and warm in order to dissolve any lead sulphate. Filter, and wash with a little hot, dilute hydrochloric acid and then thoroughly with hot water. Determine the sulphate in the filtrate as described on p. 261.

Carbonate.—In a separate portion (2 to 5 grams) of the zinc blende, determine the amount of carbonate (p. 328). Two U-tubes, each containing a concentrated solution of copper sulphate, must be placed next to the reaction flask in order to absorb the hydrogen sulphide.

ANALYSIS OF PYROLUSITE OR MANGANITE

Pyrolusite and manganite are the commonest ores of manganese. The former consists mainly of manganese dioxide, and the latter mainly of the hydrated oxide, $\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Traces of "gangue," ferric oxide, and barium oxide are usually present in both minerals.

OUTLINE OF METHOD.—One portion of the mineral is extracted with hydrochloric acid, and the *insoluble residue* of silica, etc., separated. *Barium* is separated as barium sulphate, and the *iron* is then precipitated by means of "cupferron" or by the basic acetate method. After removal of iron, the *manganese* is determined volumetrically.

In another portion of the mineral, the *manganese dioxide* is determined by a volumetric method.

Water is determined in a separate portion of the mineral.

Determination of Barium, Iron, and Manganese

To a weighed portion (about 0.5 gram) of the finely powdered mineral in a conical flask, add 10 ml. of water and 20 ml. of concentrated hydrochloric acid, and close the flask loosely with a funnel or glass bulb in order to prevent loss by spurting. Warm on the steam-bath until the residue is white, and then evaporate to complete dryness in a porcelain basin. Moisten the dry residue with concentrated hydrochloric acid, set aside for five minutes, and then dilute to about 30 ml. Filter through a small filter paper; wash the residue, and ignite it. Weigh, and report the result as "insoluble residue."

Barium.—Heat the filtrate until boiling, and to the hot solution add 1 ml. of dilute sulphuric acid. Filter, after standing, through a small filter paper, wash with hot water, incinerate the paper with the precipitate, and weigh the BaSO_4 . The quantity of barium in these minerals is so small, as a rule, that the error from the retention of ferric oxide by the barium sulphate is negligible.

Iron.—Precipitate the iron in the filtrate by means of “cupferron,” as described on p. 350. The separation from manganese of the small quantity of iron in these minerals may also be effected by a double precipitation of the iron with the minimum excess of ammonia in presence of much ammonium chloride (*cf.* p. 415), or by the basic acetate method (p. 314).

Manganese.—After the removal of iron, precipitate the manganese, and any calcium, etc., as carbonate (p. 363) after destroying cupferron. Filter, and wash thoroughly. Perforate the filter paper with a glass rod, and, by means of a jet of water, wash the precipitate into a beaker. Cover the beaker with a clock-glass, and dissolve the crude manganous carbonate in dilute sulphuric acid; wash the filter paper with a little warm dilute sulphuric acid in order to dissolve any traces of precipitate adhering to it, and add these washings to the main solution. Dilute the solution to 250 ml. and determine the manganese volumetrically in an aliquot (p. 126).

Manganese Dioxide.—In a separate portion of the mineral determine the manganese dioxide by either of the methods described under volumetric analysis (pp. 120 and 165). If the amount of manganese found in this way is less than the total manganese previously determined, calculate the excess of manganese, above that present as the dioxide, as MnO .

Water.—Determine the water in the mineral by Brush and Penfield's method (p. 404).

ANALYSIS OF A LIMESTONE OR DOLOMITE

Limestone consists essentially of calcium carbonate, but may contain also some magnesium carbonate. If the proportion of magnesium carbonate is considerable, the rock is called a dolomite. The usual minor constituents are iron, aluminium, silica (either free or combined), and sometimes traces of carbonaceous matter, phosphate, and manganese. A careful qualitative analysis must therefore precede the quantitative analysis.

In the following description of the analysis, it is assumed that a dolomite containing magnesium and calcium carbonates with small quantities of iron, aluminium, silica (or silicate), and phosphate is under examination. The results of the analysis of a rock are usually stated in terms of the constituent basic and acidic oxides, expressed as percentages. In dolomite, for example, the results are given in terms of SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , CO_2 , P_2O_5 , and H_2O , and it is convenient to tabulate them in that order.

OUTLINE OF METHOD.—The silica and silicates are separated from the remainder of the rock by treatment with hydrochloric acid. The soluble and insoluble portions are examined separately.

In the soluble portion (1) *iron* and *aluminium*, together with any phosphate, are precipitated by ammonia; (2) in the filtrate, *calcium* is determined by precipitation as oxalate; (3) after removal of the calcium, *magnesium* is determined as phosphate or oxinate.

The insoluble residue, after ignition, may be reported simply as *silica and insoluble silicates*; or, after fusion with sodium carbonate or fusion mixture, the silica may be separated, and a complete analysis made.

In separate portions of the original mineral, *carbonate*, *water*, and *phosphate* are determined.

Separation into Soluble and Insoluble Portions

Reduce about 10 grams of dolomite to a fine powder, and place the powder at once in a stoppered weighing-bottle. Take portions of this powder as required, the weight of each portion being found by difference.

Place a weighed portion (about 1.5 gram) in a porcelain basin, and cover the basin with a clock-glass to prevent loss during effervescence. Moisten the powder with a little water, and, by means of a small measuring cylinder, introduce through the spout of the basin 10 ml. of concentrated hydrochloric acid. When the action has almost ceased, rinse the cover-glass and the side of the basin with water, and boil for a few minutes. Again rinse the cover-glass and remove it. Evaporate to dryness—as far as possible on the steam-bath, and afterwards on a *gently heated* sand-bath.

Add 3 ml. of concentrated hydrochloric acid to the cold mass, and after about a minute dilute with about 10 ml. of water; warm the covered basin on the steam-bath. Filter

through a 7-cm. or 9-cm. paper and receive the filtrate in a 250 ml. beaker. Add a few drops of dilute hydrochloric acid to the basin and carefully rinse the insoluble residue into the filter with a *fine* jet of hot water. Remove any traces of silica adhering to the basin or stirring-rod with a small piece of filter paper and drop this into the filter. Rinse the basin into the filter once more, and then wash the insoluble residue about ten times with small (2 ml.) portions of hot water. A few drops of the last washing should give no turbidity with silver nitrate. The insoluble residue consists of silica and insoluble silicates; the filtrate, which should not much exceed 50 ml. in volume, contains the metallic radicals as chlorides.

Analysis of the Soluble Portion

For the most exact work, the trace of silica present in the solution must be removed by a second evaporation to dryness (p. 388), but for all ordinary purposes this is unnecessary.

Iron and Aluminium.—Add 2 ml. of concentrated nitric acid in order to oxidise any ferrous salt and to form ammonium nitrate when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 3 ml. of concentrated ammonia diluted with 5 ml. of water. Then add dilute ammonia gradually, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. (Much excess of ammonia must be avoided.) Boil for one minute. Filter, and wash three times with hot water, without necessarily bringing every trace of the precipitate on to the filter paper. Set the filtrate aside. The precipitate is mainly ferric and aluminium hydroxides (together with any phosphate), but contains also traces of calcium and magnesium salts which must be removed by reprecipitation. Dissolve the precipitate *at once* by pouring about 10 ml. of hot, dilute hydrochloric acid over the filter paper and receive the solution in the original beaker. Wash the paper a few times with hot water, and preserve it until required later. Precipitate the iron and aluminium in the filtrate as before. Filter through the same filter paper, combining the filtrate with that from the first precipitation, and wash thoroughly with a 2 per cent. solution of ammonium nitrate. Incinerate the filter paper together with the precipitate in a silica crucible without preliminary drying.

Ignite the oxides in the open, slightly inclined crucible (to allow excess of air) with a Méker burner. Cool, and weigh the Fe_2O_3 and Al_2O_3 .

The iron and aluminium in the mixed oxides are determined as follows:—Add to the crucible containing the ignited precipitate about 4 grams of potassium pyrosulphate (previously fused). Heat gently over a small flame until the salt is fused, and after any moisture has been driven off (about thirty minutes) gradually increase the temperature—care being taken to avoid boiling or spluttering—until white vapour of sulphur trioxide is slowly given off. Continue heating until the particles of precipitate have entirely disappeared, the temperature being gradually raised until, towards the end of the operation, the bottom of the crucible is at very faint redness. If the flame is removed and the crucible allowed to cool somewhat, the fused mass becomes less opaque and it is possible to see in a good light whether all the precipitate has dissolved. When no more undissolved precipitate is visible, heat for a few minutes longer and then allow the crucible to cool.

Add 2 ml. of concentrated sulphuric acid, and melt the contents of the crucible again. Cool, place the crucible in a beaker with 50 ml. of water and heat until dissolution is complete, except for a trace of silica. Remove the crucible and rinse it. Without filtering, and after cooling, determine the iron by means of decinormal permanganate after reduction by zinc amalgam (p. 141), or the silver reductor (p. 139, but see note on p. 445 if a platinum crucible was used). Calculate the weight of ferric oxide in the mixed oxides. The difference between the weight of the mixed oxides and the weight of the ferric oxide gives the weight of the alumina.

If phosphate is present, it should be determined in a separate portion of the mineral (p. 441), and a correction applied to the alumina. Calculate the phosphate as P_2O_5 , and subtract this from the weight of alumina as determined above.

Calcium.—To the combined filtrates add 1 ml. of methyl red and just acidify with dilute hydrochloric acid. Evaporate to about 200 ml.

To the gently boiling solution add 10 ml. of dilute hydrochloric acid and while continuously stirring add drop by drop a hot solution containing 3 grams of solid ammonium oxalate. Then add dilute ammonia drop by drop until the solution is

alkaline and boil for a few minutes, stirring to avoid bumping. Keep the mixture for one hour, decant the supernatant liquid through a filter, and wash three times by decantation with hot water, retaining the precipitate as far as possible in the beaker. Dissolve the impure calcium oxalate in hot, dilute nitric acid (3 ml. of concentrated acid mixed with 7 ml. of water), dilute the solution to about 200 ml., heat until boiling, and reprecipitate the calcium oxalate by adding about 2 ml. of ammonium oxalate solution and then ammonia, drop by drop, until the liquid is alkaline. Boil for a few minutes, and set the beaker aside for an hour. (If magnesium is present only in traces, one precipitation is sufficient.) Proceed according to the directions on p. 263 for the determination of calcium, filtering through the same filter as that used for the first precipitation. Combine the filtrates from the two precipitations.

Magnesium.—From the weight of calcium carbonate equivalent to the calcium oxide found, together with that of the other constituents determined, calculate the approximate magnesium oxide content, assuming that the remainder of the mineral consists of magnesium carbonate. As not more than 0.1 gram magnesium oxide should be used for the determination of magnesium, a part only of the filtrates and washings from the calcium oxalate precipitation will probably be required. If the magnesium oxide is about 20 per cent., make up the filtrates to 500 ml. in a graduated flask, and measure out 150 ml. by means of a 50 ml. pipette. If the approximate magnesium oxide content is less than 0.1 gram, use the whole of the combined filtrates.

It is necessary to remove the considerable concentration of ammonium salts present, either by evaporation to dryness, followed by gentle ignition, or better, by the careful addition of 30 ml. concentrated nitric acid, and evaporation to dryness on a water-bath. During the evaporation the nitric acid decomposes all the ammonium salts, and in the early stages loss by effervescence must be guarded against by covering the dish with a clock-glass, which must be rinsed on removal. After the ammonium salts have been driven off or decomposed, cool, and dissolve the residue, after covering the dish, by warming with 5 ml. of concentrated hydrochloric acid diluted with 20 ml. of water. Filter off any insoluble residue, and wash the dish and filter. Add methyl red, dilute to 150 ml.,

and determine the magnesium by double precipitation as phosphate as described on p. 359.

The magnesium may also be determined in a suitable volume (about one-fifth) of the filtrate from calcium by precipitation as magnesium oxinate, without the previous removal of ammonium salts (see p. 361).

Alternatively, calcium and magnesium may be determined volumetrically with EDTA by the method of Jordan and Robinson (*Chem. and Ind.*, 1953, 687).

Analysis of the Insoluble Portion

Incinerate the filter, without preliminary drying, and ignite the insoluble residue in a platinum crucible, and weigh. If the insoluble portion amounts to less than 2 per cent., it is sufficient for most purposes to report the amount as "silica and insoluble silicates"; if it exceeds that amount, analyse it according to the following scheme.

Silica.—To the insoluble residue add about six times its weight of anhydrous sodium carbonate or fusion mixture and proceed according to the directions given on p. 386 for the determination of silica in an insoluble silicate.

The filtrate from the silica may contain any of the constituents found in the soluble portion. It may be added to the main solution, or it may be analysed apart from, and in the same manner as, the main solution.

Determination of Other Constituents

Separate portions of the original mineral must be used for the determination of water, carbonate, and phosphate.

Water.—Determine the amount of water by Penfield's method, using about 2 grams of the mineral for the determination. (For details, see p. 404.)

Carbonate.—Determine the carbonate by the direct method (p. 328). Use about 1 gram of the dolomite for the determination.

Phosphate.—The amount present is often so small as to be negligible. If it is to be determined, 2 to 5 grams of the dolomite should be decomposed with dilute nitric acid. After evaporation to dryness and removal of silica, the phosphate is determined in the soluble portion by the molybdate method (p. 373), or colorimetrically (p. 304).

ANALYSIS OF AN INSOLUBLE SILICATE

(Feldspar, Clay, Mica, etc.)

Most of the natural silicates, such as clay, feldspar, garnet, and mica, are complex alumino-silicates. For example, orthoclase (potassium feldspar) may be represented as KAlSi_3O_8 ; anorthite (calcium feldspar) as $\text{CaAl}_2\text{Si}_2\text{O}_8$; albite as $\text{NaAlSi}_3\text{O}_8$; kaolinite as $\text{H}_4\text{Al}_2\text{Si}_2\text{O}_9$; and muscovite (common or potassium mica) as $\text{H}_2\text{KAl}_3(\text{SiO}_4)_3$. Pure forms of these minerals are, however, almost unknown; thus, although orthoclase has essentially the composition represented by KAlSi_3O_8 , in almost all specimens it is found that the potassium is to some extent replaced by sodium, calcium, and magnesium, whilst the aluminium is usually partially replaced by iron. Titanium is almost invariably present, and sometimes manganese. The analysis of a silicate therefore involves, as a rule, the determination of silica, aluminium, iron, manganese, titanium, calcium, magnesium, sodium, potassium, and, in some cases, phosphate, carbonate, and water.

The method about to be described in the text is usually referred to as the classical method. The name is well chosen, for the method has changed but little since the time of Berzelius. The method has many disadvantages, and in any but skilled hands may give erroneous results. In recent years an investigation has been made of the reproducibility of results in silicate rock analysis. The results of the investigation were disquieting, in that it was found that results differing over a range of several per cent. were reported. The classical method is difficult and time-consuming. For petrological purposes great accuracy is not often necessary (although it may be desirable) and the trend now is towards the development of rapid methods which have limited accuracy. Some saving in time has been achieved by working on the semi-micro scale (*i.e.* on 100 mg. samples), but the most important advance has been the use of colorimetric analysis, even for major constituents such as silica and alumina.

Full discussions and descriptions of the older methods of rock analysis will be found in Hillebrand, Lundell, Bright, and Hoffman's *Applied Inorganic Analysis*, Washington's *Chemical Analysis of Rocks*, and Groves's *Silicate Analysis*. For semi-micro and colorimetric methods the reader is referred to Guthrie and Miller, *Min. Mag.*, 1933, **23**, 405; Corey and

Jackson, *Anal. Chem.*, 1953, **25**, 624 ; Shapiro and Brannock, *U.S. Geol. Survey Circular No.* 165, 1952.

The Classical Method

OUTLINE OF METHOD.—A portion of the silicate is fused with sodium carbonate or fusion mixture and the fused mass is extracted with excess of acid. The insoluble residue is *silica*. The filtrate contains the iron, aluminium, manganese, titanium, calcium, and magnesium, which are determined as follows : *Iron*, *aluminium*, *manganese*, and *titanium* are precipitated by ammonia, the amount of iron in the mixed precipitate being determined volumetrically and the manganese and titanium colorimetrically. After removal of the iron, aluminium, manganese, and titanium, *calcium* is precipitated as oxalate. After removal of the calcium, *magnesium* is determined as phosphate.

Separate portions of the silicate are used for the determination of (1) *sodium* and *potassium* by the Lawrence Smith method ; (2) *water* ; (3) *carbonate* ; and (4) *phosphate*.

Break the mineral into small pieces on a clean steel plate. Take about 10 grams of clean pieces of the mineral, and crush in a percussion mortar to a coarse powder. Then grind to a fine powder in an agate mortar. The whole analysis is facilitated by reducing the mineral to a fine powder, but only for the determination of the alkalis is it essential to grind to the finest possible powder. A powder that will pass a 100-mesh sieve has been ground sufficiently fine. The various constituents of a rock often differ very much in hardness, and it is not permissible to reject the portion that offers most resistance to grinding, since this portion probably differs in composition from the remainder. When, therefore, *the whole* of the sample has been reduced to a fine powder, mix it thoroughly, place in a stoppered bottle, and use portions of this powder for each of the following analyses.

Determination of Silica, Iron, Aluminium, Manganese, Titanium, Calcium, and Magnesium

Fusion with Sodium Carbonate or Fusion Mixture.—Take a weighed portion (0.9 to 1.1 gram) of the powder, and fuse it with 6 grams of anhydrous sodium carbonate or fusion mixture. (For details of the procedure, see p. 386.)

Silica.—Details for the separation of the silica after the fusion are given on pp. 387 to 389.

Iron, Aluminium, Manganese, and Titanium.—Add to

the filtrate from the silica about 5 ml. of concentrated hydrochloric acid—in order to provide sufficient ammonium chloride to prevent precipitation of magnesium when ammonia is added. Heat until almost boiling and neutralise most of the acid by adding 7 ml. of concentrated ammonia diluted with 7 ml. of water. Then add dilute ammonia, drop by drop, until a faint ammoniacal odour persists after stirring and blowing away the ammonia vapour. Add 1 gram of pure ammonium persulphate, heat to boiling, and add dilute ammonia until it is present in *slight* excess. Boil for a few minutes, adding ammonia when necessary to keep the solution alkaline. Following the procedure described under Dolomite (p. 438), filter off and wash the precipitate (use an 11-cm. paper if necessary), dissolve at once in hot 2N hydrochloric acid, and reprecipitate with ammonia as before. Add a *small* quantity of well-washed paper-pulp (see p. 45) and boil for about a minute. (The paper-pulp facilitates the washing of the precipitate, its reoxidation during ignition, and especially its subsequent dissolution in fused pyrosulphate.) Filter off and wash the precipitate with a 2 per cent. solution of ammonium nitrate until free from chloride. Ignite with a Méker burner and weigh the mixture of Mn_3O_4 , Fe_2O_3 , Al_2O_3 , P_2O_5 , and TiO_2 in the platinum crucible containing the non-volatile residue from the silica (see p. 389).

Add to the crucible containing the ignited precipitate about 10 grams of powdered potassium pyrosulphate (previously fused), and proceed with the fusion as described on p. 439.

Add 5 ml. of concentrated sulphuric acid and melt the contents of the crucible again. Cool, place the crucible with about 100 ml. of water in a beaker, and heat gently. When the crucible is free from adhering sulphate, remove and rinse it. If the fusion has been successful, only traces of silica remain undissolved. Filter through a small paper and wash the silica. Ignite and weigh the silica in a platinum crucible, correct it for impurity (p. 389), and add the amount to the weight of the main silica precipitate. After volatilising the silica, fuse the slight residue in the crucible with a small piece of pyrosulphate, and add this to the main solution for the determination of iron, aluminium, manganese, and titanium.

Manganese.—Make up the filtrate to 250 ml. in a graduated flask, and remove with a pipette 50 ml. for the colorimetric determination of manganese as described on p. 302.

Iron.—Transfer 100 ml. of the solution remaining in the graduated flask to a larger flask. Reduce the iron to the ferrous state by means of hydrogen sulphide, or the silver reductor,¹ and determine the iron volumetrically with potassium permanganate (p. 143) or ceric sulphate (p. 152) respectively.

Titanium.—Transfer 50 ml. of the solution to a 100 ml. graduated flask. Add 1 ml. of phosphoric acid and 10 ml. of hydrogen peroxide, and dilute to the graduation mark. Determine the titanium colorimetrically (p. 306).

Aluminium.—From the total weight of the mixed oxides deduct the weights of Fe_2O_3 , TiO_2 , Mn_3O_4 , and SiO_2 obtained as above. The weight of Al_2O_3 is thus found. (If phosphate is present, it is determined in a separate portion of the mineral (p. 448) and the corresponding weight of P_2O_5 is deducted from the weight of alumina.)

Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 439).

Determination of Sodium, Potassium, and Lithium

(*Lawrence Smith Method*)

OUTLINE OF METHOD.—The silicate is decomposed by heating with ammonium chloride and calcium carbonate. The mass is extracted with water, and a solution of the chlorides of calcium, lithium, sodium, and potassium is obtained. The calcium is removed, partly as carbonate and the remainder as oxalate. The sodium, potassium, and lithium are then determined in the usual manner.

The ammonium chloride must be pure, and it is advisable to sublime a portion for the special purpose of this determination. The calcium carbonate must be specially purified. The purest obtainable calcium carbonate (or pure calcspar) is dissolved in hydrochloric acid contained in a porcelain basin. Excess of ammonia is added to the solution which is heated almost to the boiling-point, and a freshly prepared solution of pure ammonium carbonate is then added. The precipitate is

¹ If the silver reductor is used, and the ferrous iron is titrated with ceric sulphate, with *o*-phenanthroline ferrous complex as indicator, a "returning" end-point will be observed. This arises from the slow oxidation of platino-chloride produced by reduction of platinichloride derived from platinum dissolved during the pyrosulphate fusion. The first sharp colour change represents the true end-point.

collected in a Büchner funnel, washed *very thoroughly* with hot water, and dried. Even after this purification, it may still contain traces of alkali metals, derived probably from the vessels employed. A "blank" experiment must therefore be carried out with the same quantities of the reagents and in the same manner as in the actual analysis, and the necessary correction applied in subsequent analyses. If the weight of alkali chloride from 0.5 gram of ammonium chloride and 4 grams of calcium carbonate exceeds 2 mg., further purification of the reagents is necessary.

For a successful determination of the alkali metals, it is in most cases essential that the substance should be ground to the finest possible powder. If the mineral contains much alumina, the powder must be passed through a 200-mesh sieve. When mica is present, it cannot be reduced to a very fine powder on account of its ready cleavage into plates and the flexibility of these plates; mica, however, is more readily decomposed than most silicates, and less thorough grinding suffices for it.

A special finger-shaped platinum crucible is most suitable for the ignition, but an ordinary 30 ml. platinum crucible is quite satisfactory. Certain precautions are necessary to prevent loss of the alkali chlorides by volatilisation. The crucible, with a well-fitting lid, should be supported on a perforated asbestos screen (p. 236) so that the lowest third, but not more, can be heated to a red heat.

Decomposition of the Silicate.—Weigh, by difference, about 0.5 gram of the silicate into a platinum basin or a large agate mortar. Add 0.5 gram of ammonium chloride and mix the powders very thoroughly by gentle rubbing and stirring with a small agate pestle. Weigh approximately 4 grams of calcium carbonate, add most of this to the basin, and continue the stirring and rubbing until thorough mixing has resulted. Place the platinum crucible on a sheet of glazed paper and put into it sufficient calcium carbonate to cover the bottom in order to prevent adhesion of the mass after the ignition. With the aid of a small spatula, transfer the mixture very carefully from the basin to the crucible. "Rinse" the basin, and clean the spatula with the remainder of the calcium carbonate and add this to the crucible, together with any powder that has fallen on the glazed paper.

Support the covered crucible in a hole of appropriate size

cut in asbestos board, and heat with a small flame for about ten minutes. When the odour of ammonia is no longer perceptible, increase the flame until the lower part of the crucible is heated somewhat above dull redness, and continue the heating for about forty minutes. In the case of minerals rich in alumina, the temperature must finally be raised to a bright red heat for fifteen minutes.

Allow the crucible to cool. Add 3 ml. of water to slake the quicklime that has been formed and to disintegrate the mass. After a few minutes transfer the contents of the crucible to a porcelain basin, detach any adhering portions with a platinum spatula (or a plastic rod), and rinse the crucible with about 50 ml. of hot water. Use a wash-bottle of resistant glass. Carefully break down any lumps with an agate pestle, and boil gently for a few minutes. Filter into a beaker of resistant glass, and wash the residue thoroughly with about 150 ml. of hot water. The solution contains all the alkali chloride, together with some calcium chloride.

Removal of Calcium.—To the hot solution add 10 ml. of ammonia, and about 2 grams of ammonium carbonate dissolved in cold water. Filter into a 15-cm. porcelain basin, and wash the calcium carbonate thoroughly with hot water. To recover occluded traces of alkali metals, dissolve this precipitate in the least possible amount of dilute hydrochloric acid. Dilute the solution, and reprecipitate the calcium carbonate. Filter, wash, and combine the filtrates. Evaporate the filtrates to about 50 ml., transfer to a platinum basin, and evaporate to complete dryness on the steam-bath. Heat the covered basin in an air-oven at 140° for an hour, and then expel ammonium salts by gentle ignition (see p. 384).

The residue still contains traces of calcium and possibly sulphate, which are removed as follows :—Dissolve the residue in 3 to 4 ml. of water ; add 1 drop of barium chloride, 1 ml. of ammonium carbonate, and a few drops of ammonium oxalate. Evaporate almost to dryness on the steam-bath. Add 3 to 4 ml. of water, filter through a small paper into a weighed platinum crucible, and wash the basin and the filter 6 to 8 times with warm water, using about 2 ml. at a time. Add a drop of hydrochloric acid to the crucible, evaporate to dryness, and expel ammonium salts by gentle ignition. Finally, heat the bottom of the crucible to very faint redness (barely visible in

direct daylight), rotating the Bunsen flame round the crucible, care being taken to avoid actual fusion of the alkali chlorides. Cool, and weigh.

Determination of Sodium, Potassium, and Lithium.—The weight of the residue gives the weight of the mixed sodium, potassium, and lithium chlorides. If lithium is present, this metal is first separated from sodium and potassium as described on p. 356. In the absence of lithium, the mixed chlorides of sodium and potassium are analysed as indicated on p. 383. For very accurate work, impurity derived from the reagents, glass vessels, etc., should be determined by carrying out a "blank" experiment. It may be assumed without serious error that the impurity consists of sodium chloride only.

Note.—If the mixed chlorides do not dissolve completely in water, collect the insoluble residue on a small filter paper, wash with hot water, ignite, and weigh. If the weight is less than 1 mg., subtract it from that of the mixed chlorides; if more than 1 mg., reject the analysis.

Determination of Water, Carbonate, and Phosphate

Water and Carbonate.—Use separate portions of the powdered mineral for the determination of (1) water, as described on p. 404; and (2) carbonate, as described on p. 328. Many silicates contain no carbonate, but it is often found in clays.

Phosphate.—Weigh accurately about 1 gram of the powdered mineral into a small platinum basin. Add 10 ml. of water and mix thoroughly by stirring with a platinum wire. Then add 10 ml. of concentrated nitric acid and 5 ml. of hydrofluoric acid. Evaporate to dryness on the steam-bath. Add 5 ml. of nitric acid, evaporate again and repeat the evaporation with nitric acid two or three times in order to decompose fluorides. Heat the dry residue until it becomes brown, add 15 ml. of dilute nitric acid and boil gently for a few minutes in order to convert any meta- or pyrophosphate into orthophosphate. Filter, and wash with warm, dilute nitric acid. Determine the phosphate in the solution by the molybdate method (p. 373).

ANALYSIS OF A GLASS

Ordinary "soft" glass, used for bottles, window glass, etc., is essentially a sodium-calcium silicate; in "hard" glass the sodium is replaced by potassium. Flint glass is a potassium-lead silicate. Pyrex glass contains about 12 per cent. of boric oxide, and Jena glass is a sodium-zinc borosilicate. Aluminium and traces of iron, manganese, and magnesium are present in most glasses. Oxides of cobalt, copper, iron, chromium and manganese are used in the preparation of coloured glasses. Bone ash, cryolite, or fluorspar is added to common glass in order to render it opaque.

The commonest constituents of glass are therefore silica, sodium, potassium, calcium, lead, and aluminium, with traces of iron, manganese, and magnesium. The analysis of a glass is therefore carried out according to the procedure for an insoluble silicate, but when lead and manganese are present the method must be modified as follows:—

OUTLINE OF METHOD.—The glass is fused with sodium carbonate or fusion mixture and the fused mass is extracted with hydrochloric acid. *Silica* is determined in the insoluble residue. In the filtrate from the silica, the *lead* is precipitated as sulphide. After removal of lead, the *iron*, *aluminium*, and *manganese* are precipitated together by means of ammonia and ammonium persulphate and weighed as oxides; the iron in the mixed oxides is determined volumetrically. After removal of iron, aluminium, and manganese, *calcium* is precipitated as oxalate and *magnesium* as phosphate.

Separate portions of the glass are used for the determination of (1) *manganese* by the bismuthate method, (2) *sodium* and *potassium* by the Lawrence Smith method, (3) hygroscopic *water*.

Fusion with Sodium Carbonate or Fusion Mixture, and Determination of Silica.—Fuse a weighed portion (about 1 gram) of the finely powdered glass with sodium carbonate or fusion mixture, as described on p. 386. (If the glass contains lead, great care must be taken to maintain an oxidising atmosphere within the crucible, in order to avoid reduction of lead compounds and consequent serious damage to the crucible. The crucible must be placed on the triangle in a slightly inclined position so that the flame does not completely envelop it; and the sodium carbonate or fusion mixture must be free from organic impurities, such as traces of paper and straw. A few centigrams of potassium nitrate may be

mixed with the sodium carbonate or fusion mixture in order to minimise the risk of reduction.) After dehydrating the silica, wash the insoluble residue with hot, dilute hydrochloric acid and then *very thoroughly* with hot water, since the lead chloride is somewhat difficult to remove. Test the purity of the silica in the usual manner, keeping the non-volatile residue.

Lead.—To the filtrate from the silica (about 150 ml.) contained in a 400 ml. conical flask, add moderately concentrated ammonia until a faint turbidity is obtained. Then add 5 ml. of concentrated hydrochloric acid. (In order to secure complete precipitation of the lead, the concentration of acid in the solution must not much exceed 0.3N.) Heat the solution to about 60° and saturate with hydrogen sulphide. Filter, and wash the precipitate with very dilute hydrochloric acid containing hydrogen sulphide. The precipitate, which may be light brown in colour on account of admixed sulphur, invariably contains a trace of platinum sulphide derived from the crucible in which the fusion was made.

Dissolve the lead sulphide by pouring 20 ml. of boiling 5N hydrochloric acid into the filter in small portions, and receive the solution in a porcelain basin; wash the filter with hot water. Following the procedure described on p. 354, determine the lead in the solution as lead sulphate.

If only traces of lead are present, evaporate the lead chloride solution nearly to dryness, dilute to 100 ml. in a standard flask, and determine the lead colorimetrically (see, for example, Sandell, *Ind. Eng. Chem., Anal. Ed.*, 1937, 9, 464).

Iron, Aluminium, and Manganese

Evaporate the filtrate from the lead sulphide to 100 ml. and transfer it to a 250 ml. beaker. Add 3 ml. of concentrated nitric acid (to oxidise ferrous salt and to provide sufficient ammonium salt when ammonia is added) and heat until boiling. Remove the flame and neutralise most of the acid by adding 5 ml. of concentrated ammonia diluted with 5 ml. of water. Add 1 gram of ammonium persulphate, heat until boiling, and then add dilute ammonia until the solution is distinctly ammoniacal. Boil for not more than two minutes, and make sure that a faint ammoniacal odour persists.

Filter through a 9-cm. or 11-cm. paper (according to the amount of precipitate) and wash with a little hot water. Set

the filtrate aside. Dissolve the precipitate in 10 to 20 ml. of hot 5N hydrochloric acid containing a few drops of sulphurous acid and receive the solution in the original beaker. Wash the filter paper. Reprecipitate with ammonia and ammonium persulphate, and add a small quantity of ashless paper pulp (p. 45). Filter, and wash thoroughly with hot water. Ignite the precipitate (with a Méker burner) in the platinum crucible containing the non-volatile residue from the silica (p. 389), and weigh the mixture of Fe_2O_3 , Al_2O_3 , Mn_3O_4 , and a trace of SiO_2 .

Iron.—Fuse the mixed oxides with potassium pyrosulphate as described on p. 439. Separate and weigh the silica that is always found here (see p. 444), and determine the iron volumetrically with centinormal permanganate, or colorimetrically. Calculate the percentage of Fe_2O_3 in the glass and also the weight of Fe_2O_3 in the mixed oxides.

Manganese.—Place a weighed portion (about 1 gram) of the finely powdered glass in a platinum basin. Add 10 ml. of sulphuric acid (1 : 1) and 5 ml. of hydrofluoric acid, and mix thoroughly by stirring with a stout platinum wire. Warm the mixture gently in the fume cupboard, with frequent stirring, and then evaporate as far as possible on the steam-bath. Remove the basin to a sand-bath and heat more strongly until fumes of sulphuric acid are evolved. Cool, add 3 ml. of concentrated sulphuric acid, dilute with a little water, and heat for a few minutes to dissolve soluble sulphates. Transfer the contents of the basin to a conical flask, dilute to 100 ml., and heat until almost boiling. (As a rule the sulphates dissolve completely—except possibly lead sulphate.) Cool to 40° , and determine the manganese in the solution by the bismuthate method as described on p. 128 for manganese in iron ore. The manganese may also be determined colorimetrically. Calculate the percentage of MnO in the glass, and also the weight of Mn_3O_4 in the mixed oxides.

Aluminium.—Deduct the weights of Fe_2O_3 , Mn_3O_4 , and SiO_2 (obtained as above) from the total weight of the mixed oxides. The weight of the Al_2O_3 in the oxides is thus obtained and the percentage of Al_2O_3 in the glass may then be calculated.

Calcium and Magnesium.—In the filtrate from the iron, etc., determine the calcium and magnesium as described under the analysis of Dolomite (p. 439).

Sodium and Potassium.—In a separate portion of the glass (about 0.5 gram) determine the sodium and potassium by the Lawrence Smith method (p. 445).

Water.—Glass powder is very hygroscopic, and it is advisable to determine the “hygroscopic water” by Penfield’s method (p. 404), and to express all other results as percentages of the dry glass. Analyses of the same sample made at different times will then be comparable.

ANALYSIS OF PORTLAND CEMENT

Portland cement is an instance of a silicate most of which can be decomposed by means of acid, rendering the process of fusion with carbonate unnecessary. The constituents are silica, lime, alumina, and ferric oxide, with small amounts of oxides of alkali metals, magnesia, sulphur trioxide, and carbon dioxide. It may also contain traces of the oxides of titanium, manganese, and phosphorus, which are not usually determined separately.

OUTLINE OF METHOD.—The sample is decomposed by hydrochloric acid, and the silica rendered insoluble by evaporation and dehydration. The iron and aluminium (with any manganese, titanium and phosphate) are precipitated by ammonia, the amount of iron in the precipitate being determined volumetrically, and the aluminium calculated by difference. After the removal of these constituents, the calcium is precipitated as oxalate, and the magnesium subsequently determined as phosphate. Alkali metals are determined by the Lawrence Smith method on a separate portion of the sample. The sulphur trioxide is determined as barium sulphate on a further portion of the sample, which is also used for the determination of undecomposed constituents. The amounts of carbon dioxide and moisture are found by strong ignition of a larger portion of the sample.

Silica.—Weigh accurately between 0.5 and 0.6 gram of the sample into a porcelain dish, add 20 ml. of water, mix with a stirring-rod, and add 20 ml. of concentrated hydrochloric acid. Cover the dish, and heat on a water-bath until the cement is decomposed. Rinse the cover-glass, and continue the evaporation to dryness, stirring frequently towards the end. Dehydrate the silica, extract the basic constituents, and determine the amount of silica as described on pp. 386-389.

Iron and Aluminium.—In the filtrate from the silica, determine the iron and aluminium by double precipitation with

ammonia (and, if necessary, the manganese and titanium) as described under feldspar (p. 443).

Calcium.—In the combined filtrates from the iron and aluminium, determine the calcium by double precipitation as oxalate as described under Dolomite (p. 439).

Magnesium.—The magnesium in the whole of the combined filtrates from the calcium determination is precipitated as magnesium ammonium phosphate, and converted to magnesium pyrophosphate as described under Dolomite (p. 440).

Alkali Metals.—In a separate portion of the cement, in weight about 1 gram, determine the sodium and potassium by the Lawrence Smith method (p. 445).

Sulphur Trioxide, and Undecomposed Constituents.—Weigh accurately about 0.5 gram of the cement, and decompose it with hydrochloric acid as described above. Evaporate the solution to dryness on the water-bath, and, without further dehydrating the silica, extract the basic constituents with hydrochloric acid, filter, and wash the silica. Keep the filtrate for the sulphur trioxide determination.

The silica is washed back into the dish used for the decomposition of the cement or (better) into a platinum dish, and enough sodium carbonate added to give approximately a 5 per cent. solution. The dish is then heated on a water-bath for about an hour to extract the free silica. Filter the solution, wash the undecomposed residue, ignite, and weigh.

The filtrate which has been kept for the sulphur trioxide determination is heated to boiling, and the sulphate precipitated by barium chloride solution as described on p. 261. In order to calculate the amount of barium chloride required, assume that the cement contains about 3 per cent. of sulphur trioxide.

Loss on Ignition.—Weigh out about 1 gram of the sample, and heat strongly in a platinum crucible, which should be supported in a hole cut in an asbestos board. Cool, weigh, and repeat the ignition until the weight is constant.

ANALYSIS OF SUPERPHOSPHATE MANURE

Superphosphate manure is prepared from natural phosphate by treatment with sulphuric acid. By this treatment, insoluble tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, is converted into

soluble acid phosphate, $\text{CaH}_4(\text{PO}_4)_2$. The value of a superphosphate as a plant fertiliser depends mainly on the amount of soluble phosphate present. It is therefore often sufficient to determine only the respective amounts of "soluble" and "insoluble" phosphates. The following scheme for a more complete examination of a superphosphate is sufficiently comprehensive for most purposes.

OUTLINE OF METHOD.—Separate portions of the superphosphate are used for the determination of (1) "Siliceous matter," iron, aluminium, and calcium; (2) Soluble phosphate; (3) Total phosphate; (4) Sulphate; (5) Water, organic matter, sodium, and potassium.

The sample should be thoroughly mixed in order to secure uniformity, but it should not be dried or ground. All results should be expressed in percentages of the original, undried material.

Determination of Iron, Aluminium, and Calcium

Place about 2.5 grams (accurately weighed) of the superphosphate in a porcelain basin, add 20 ml. of water, 10 ml. of concentrated hydrochloric acid, and 1 ml. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness, first on the steam-bath and then on a *gently heated* sand-bath. Add 5 ml. of concentrated hydrochloric acid to the dry residue and warm gently; then add 30 ml. of water and heat for a few minutes. Filter, wash the insoluble residue with hot dilute hydrochloric acid and then thoroughly with hot water. Ignite, and weigh the "insoluble residue."

Add sodium carbonate to the filtrate until it is alkaline (avoid loss due to effervescence), then add a few crystals of potassium nitrate and evaporate to dryness in a porcelain basin. Ignite the residue gently in order to destroy organic matter. Allow to cool. Dissolve the residue by warming with 10 ml. of concentrated hydrochloric acid diluted with 30 ml. of water. Transfer the solution (after filtering if necessary) to a 250 ml. standard flask, cool, and dilute to the mark.

Iron and Aluminium.—(a) Measure 50 ml. of the solution into a 600 ml. beaker, add 10 grams of ammonium chloride, 2 ml. of methyl orange, and ammonia until alkaline. Then add dilute hydrochloric acid, drop by drop, until just acid.

Dilute to about 400 ml., heat until boiling, add 3 grams of ammonium acetate, and boil for two minutes. Filter, and wash with a little hot water. Dissolve the precipitate in hot dilute hydrochloric acid, and receive the solution in the original beaker. Wash the filter paper. Add 10 grams of ammonium chloride to the solution, neutralise the excess of acid as before, dilute to 300 ml., and reprecipitate with ammonium acetate. Filter and wash with hot 2 per cent. ammonium acetate solution. Incinerate the paper, and ignite the precipitate in an open crucible with a Méker burner. Weigh the mixture of FePO_4 and AlPO_4 .

(b) In another portion (100 ml.) of the solution determine the iron volumetrically. Reduce the ferric salt with zinc (p. 137) and titrate with 0.02N permanganate, or with stannous chloride (p. 143) and titrate with 0.02N dichromate (p. 144).

Calcium.—Mix the filtrates from the two precipitations of iron and aluminium phosphates and (without evaporation) precipitate the calcium as oxalate by adding drop by drop a hot solution containing 2 grams of ammonium oxalate (but no ammonia) to the boiling solution. Filter, wash the precipitate, convert it to calcium oxide, carbonate, or sulphate, and weigh (pp. 263, 264).

Determination of Soluble and Total Phosphate

Soluble Phosphate.—Place 5 grams of the superphosphate in a 500 ml. measuring flask and add 400 ml. of water. Shake vigorously by means of a shaking machine for thirty minutes. Dilute the solution to 500 ml. and, after mixing, filter part of the turbid mixture. (Reject the first portion of the filtrate.) Determine the phosphate in 10 ml. of the filtrate (corresponding to 0.1 gram of the superphosphate) by the molybdate method, either gravimetrically (p. 373) or volumetrically (p. 111).

Total Phosphate.—Place a weighed portion (about 2 grams) of the superphosphate in a porcelain basin, add 25 ml. of water and 10 ml. of concentrated nitric acid, and boil gently in the covered basin for about five minutes. Evaporate to dryness, first on the steam-bath, and then on a *gently* heated sand-bath. Add 5 ml. of concentrated nitric acid to the residue and warm gently; then add 30 ml. of water and heat for a few minutes. Filter, and wash the insoluble residue with hot dilute nitric

acid and then with hot water. Dilute the solution, after cooling, to 500 ml. in a standard flask. Determine the phosphate in 25 ml. of the solution by the molybdate method.

Insoluble Phosphate.—The difference between the total phosphate and the soluble phosphate (expressed as percentages of P_2O_5) gives the percentage of P_2O_5 present as insoluble phosphate.

Alternatively, the soluble and insoluble phosphate may be determined by Wilson's volumetric methods (*Analyst*, 1954, 79, 535).

Determination of Sulphate

Extract a weighed portion (0.5 to 1 gram) of the superphosphate with hydrochloric acid, evaporate to dryness, and prepare a solution as described on p. 454. In the filtrate from the insoluble residue, determine the sulphate as described on p. 261.

Determination of Water, Organic Matter, Sodium, and Potassium

Water.—Spread in a thin layer a weighed portion (2 to 5 grams) of the superphosphate in a platinum basin, and dry for five hours at 100° . Report the loss of weight as "moisture."

Place the dried sample in an air-oven, and dry at 160° to 170° until the weight is constant. Report the further loss of weight as "combined water."

Organic Matter.—To the dried residue, add saturated barium hydroxide solution, mixing thoroughly with a glass rod, until the solution is alkaline. Evaporate to dryness on the steam-bath, and dry at 160° to 170° until the weight is constant. Then heat on a sand-bath, gently at first, and finally for fifteen minutes to barely visible redness. Cool in a desiccator, and weigh. The loss of weight resulting from the ignition is the weight of the organic matter.

Sodium and Potassium.—If sodium and potassium are to be determined, it is convenient to use the residue after the treatment above. Proceed in the same manner as with the ignited mass obtained in the determination of the alkali metals by the Lawrence Smith method (p. 445).

PART VII

GAS ANALYSIS

THE analysis of a gas is usually conducted in one of two ways.

(1) A measured volume of the gas is treated with a suitable absorbing-reagent and the change of volume noted, or

(2) A measured volume of the gas is treated with a suitable reagent, and the constituent thus absorbed is then determined in the reagent. This is the usual method for the determination of traces of one constituent, since large volumes of gas may be used; it is also the general method for gases that are readily soluble in water, such as sulphur dioxide.

In practice, gases are generally measured in contact with mercury or water. The vapour pressure of mercury is so small at ordinary temperatures that it may be neglected except in the most exact work. The vapour pressure of water is much greater, and it cannot be neglected in accurate work. As a rule, a gas is measured in the moist state at the room temperature and at barometric pressure, and corrections are then applied to find the volume the gas would occupy in the dry state at 0° and 760 mm. If v is the observed volume of the gas, t its temperature in $^{\circ}\text{C}.$, p the barometric pressure in mm., and w the vapour pressure of water at temperature t , the corrected volume, V , is found from the following equation:—

$$V = v \frac{(p-w) 273}{760 (273+t)}.$$

For work of high precision the temperature of the barometer should be read, as a change in temperature of 25° from the standard temperature $0^{\circ}\text{C}.$ will cause an error of nearly 0.5 per cent. The corrected pressure, P_o , is given by the following equation:—

$$P_o = P[1 - (\alpha - \beta)t]$$

in which P is the pressure observed in mm., α the coefficient of

expansion of mercury (0.00018), β the coefficient of expansion of brass (0.000018), and t the temperature of the barometer. If this equation is used it will be found that the correction to be subtracted from the observed pressure is approximately 1 mm. at 8° , 2 mm. at 16° , 3 mm. at 24° , and 4 mm. at 31° .

Technical Methods.—Analyses can be performed rapidly and with sufficient accuracy for many purposes by using apparatus (designed mainly by Hempel) with water as the confining liquid. In these analyses the corrections mentioned above are neglected, since the error introduced in this way is not larger than other errors inherent in the methods. It is assumed, in fact, that the temperature and pressure remain constant during the analysis. Any variation in the barometric pressure that may occur during an analysis is usually negligible, but care is necessary if the temperature variation is to be kept within sufficiently narrow limits. Obviously, the temperature will alter if any of the apparatus is brought near a flame, or is exposed to direct sunlight. For the same reason the apparatus must be lifted by the support, and the glass parts must not be touched more than is necessary with the hands.

A number of complex types of apparatus for accurate gas analysis are now available. In some of these the volume of the gas being analysed is maintained constant, and its pressure determined before and after absorption of the various constituents. In the following account only the more easily available forms of apparatus are described.

COLLECTION OF A SAMPLE OF GAS FOR ANALYSIS

If a large quantity of the gas is available, it is most convenient to fill a tube or other vessel with it by displacement of the air originally present, care being taken that the air is completely displaced.

When the quantity of gas is limited, the receiver must be filled with water or mercury which is then displaced by the gas. An inverted wash-bottle with a piece of rubber tubing and a screw-clip on each of the tubes may be used for the collection of a gas (Fig. 75). In the laboratory it is usually

possible to collect the gas directly in the gas-burette (see p. 461).

Samples of air in mines, etc., are conveniently collected in small (100 to 200 ml.) glass-stoppered bottles. To collect the sample, remove the stopper, insert a rubber stopper fitted with inlet and outlet tubes, and blow the air through the bottle by means of a small bellows or other simple air-pump. Withdraw the rubber stopper, and immediately insert the glass stopper which is lubricated with vaseline to render the bottle air-tight. Fix the stopper in position by means of a stout rubber band. The transference of the gas from the bottle to a gas-burette is described on p. 462. Instead of using a stoppered bottle, the sample may be collected in a glass tube with a tap at each end.

In connection with both the collection and the analysis of a gas, two points require special mention, viz., the solubility of gases in water and aqueous solutions, and the permeability of rubber to gases. The solubility of nitrogen and oxygen is too small to affect an analysis seriously, particularly as the reagents are already saturated with these gases at their respective atmospheric partial pressures. With most other gases, the reagents should be saturated with each gas present in the mixture, at the pressure corresponding to its partial pressure. This is accomplished with sufficient exactness for most purposes by carrying out several successive analyses of the same sample; the error from this source will then diminish with each successive analysis, and the second or third analysis should be sufficiently accurate. Carbon dioxide, however, is so soluble that it cannot be accurately determined with any apparatus in which water is the confining liquid. Mercury is suitable for most gases which are soluble in water, but it cannot be used if chlorine, nitrogen peroxide, or hydrogen sulphide is present, as these gases react with the metal.

Although rubber is impermeable to water, it is not impermeable to gases. All gases will pass through a rubber membrane even if it is free from flaws. The rate of diffusion through rubber varies with different gases, and is fast enough with

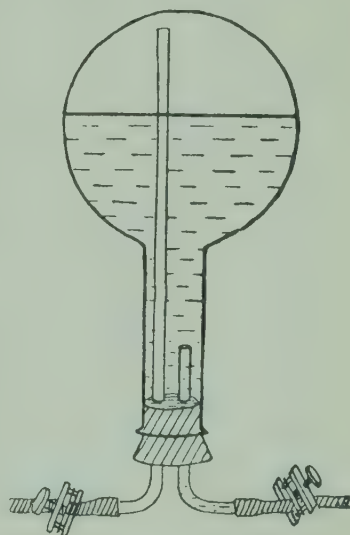


FIG. 75.

carbon dioxide to introduce a serious error if the gas is exposed for any considerable time to a rubber wall. In practice, therefore, all rubber connections are kept as short as possible, and bound with wire where practicable. Old or parched rubber should never be used, and all rubber tubes should be tested for leaks from time to time. Clips of any kind should be removed when the apparatus is not in use.

Gas Analysis with the Hempel Apparatus

THE sample of gas to be analysed is introduced into a gas-burette, in which it is measured. It is then led into a gas-pipette, in which it is treated with a reagent which absorbs one constituent of the mixture. The residue is brought back

into the gas-burette and the volume again measured, the contraction giving the volume of the constituent absorbed. The residue is then led into another gas-pipette, where it is treated with another reagent which absorbs a second constituent, and the residual gas is again brought back to the burette for measurement. This series of operations is continued, using as many pipettes as there are constituents to be determined.

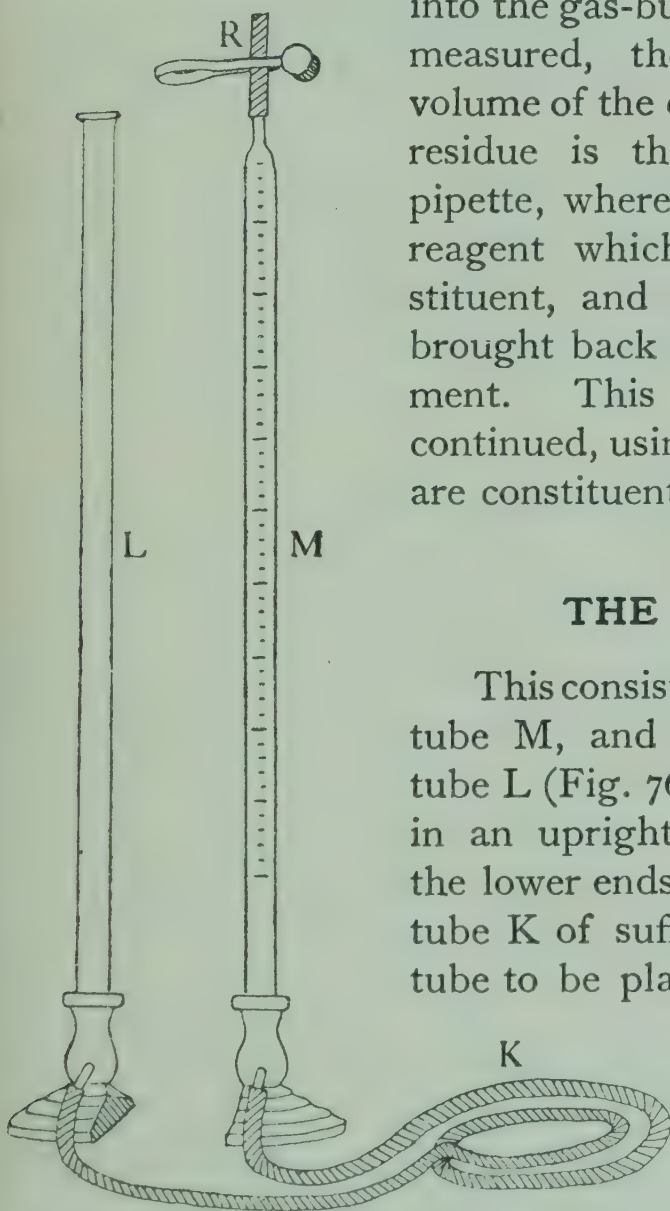


FIG. 76.

THE GAS-BURETTE

This consists of a graduated measuring-tube M, and an ungraduated levelling-tube L (Fig. 76). Each tube is supported in an upright position by a stand, and the lower ends are connected by a rubber tube K of sufficient length to allow one tube to be placed on the floor while the other is on the working bench.

The measuring-tube is graduated in fifths of a millilitre, from 0 to 100 ml. It terminates at the upper end

in a short capillary tube to which a rubber tube R is attached. This rubber tube should be securely wired on to the glass

capillary tube, leaving about 3 cm. of the rubber tube projecting.

To prepare the burette for an analysis, pour into the levelling-tube sufficient water to fill *one* of the glass tubes and the connecting rubber tube. In order to make sure that there is no air in the rubber tube, run the water to and fro in the tubes by alternately raising and lowering one of them. Then raise the levelling-tube until the measuring-tube and rubber tube R are completely filled with water, and close the rubber tube with a clip, placed as near the glass as possible.

Introduction of a Sample into the Burette.—Fill the measuring-tube with water as described above, and close the clip on the tube R. If the rubber tube R is not quite full, fill it from a wash-bottle. Insert into the rubber tube a well-fitting, capillary-bored, glass tube leading from the vessel containing the gas to be analysed. All air in the leading-tube must have been previously expelled by passing some of the gas through it, or by filling it with water. Open the clip on the tube R and, by lowering the levelling-tube, allow the gas to enter until the burette contains a little more than 100 ml. Close the clip on R, and disconnect the leading-tube.

It is convenient to work with exactly 100 ml. of gas, and this is readily measured off in the following manner. Wait for two minutes until the water has drained from the side of the measuring-tube, then raise the levelling-tube until the gas is compressed to slightly less than 100 ml. and close the rubber connecting-tube K by pinching between the fingers. Lower the levelling-tube and, by cautiously relaxing the pressure of the fingers on the tube K, allow the gas to expand until the volume is exactly 100 ml.; then pinch the rubber tube tightly again and open the clip on R for a moment. The excess of gas thereby escapes, leaving exactly 100 ml. at atmospheric pressure. Make sure that the volume is exactly 100 ml. by equalising the levels of the water in the two tubes of the burette and reading the volume of gas. When adjusting the water levels, hold the levelling-tube in a sloping position and bring it into contact with the measuring-tube. The measuring-tube must be vertical.

The operation of introducing exactly 100 ml. of gas into the burette should be practised with air.

Introduction of a Sample from a Small Bottle.—Hold the mouth of the bottle below the surface of some mercury contained in a deep trough. Remove the stopper, care being taken that the mouth of the bottle is kept well below the

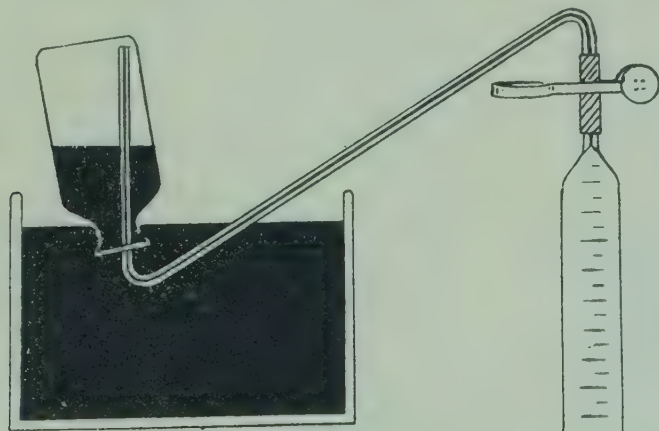


FIG. 77.

surface of the mercury, and that no air is trapped at the rim of the bottle. Fill a bent, thick-walled, capillary tube with water, insert it into the bottle, and connect the other end of the capillary tube with the gas-burette (Fig. 77). The burette may then be filled as described above.

ABSORPTION PIPETTES

Simple Absorption Pipette for Liquids.—This consists of two glass bulbs, A and B, connected by a tube. The bulb A is of about 150 ml. capacity and is connected with a long capillary tube C, which is bent as shown in Fig. 78. The bulb B must not be less than 120 ml. capacity. The pipette is supported on a metal or wooden stand. A short piece of good rubber tubing is wired on to the open end of the capillary tube. When the pipette is not in use, this rubber tube should be closed with a glass plug, and the tube D should be closed with a small rubber stopper.

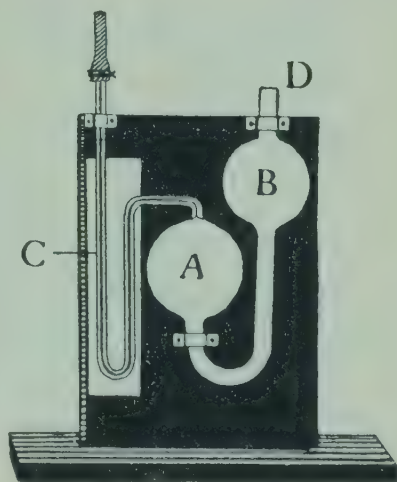


FIG. 78.

The pipette is filled by running in, through the tube D, sufficient of the reagent to fill the bulb A completely and the bulb B to a depth of about 1 cm.

Simple Absorption Pipette for Solids or Liquids.—This differs from the form above in having a tube at E (Fig. 79) through which a solid reagent may be introduced into the absorption bulb A. The tube E is closed with a rubber stopper

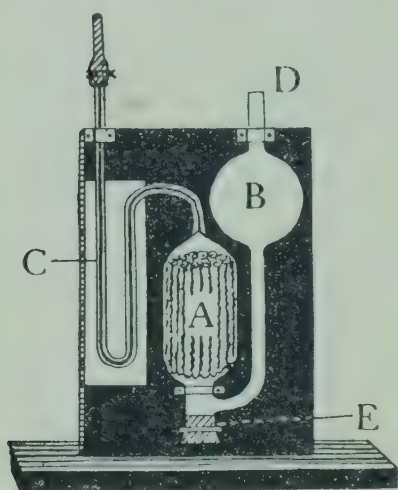


FIG. 79.

which should be securely wired in place. With this pipette, absorption with liquid reagents can be greatly facilitated by packing the bulb A with rolls of wire gauze or with fine glass rods before filling the pipette with the reagent. When the gas is then introduced into A, it is exposed to a large surface of the reagent.

Double Absorption Pipettes.—

Reagents, such as cuprous chloride, alkaline pyrogallate, etc., which absorb oxygen, must not be used in the simple pipettes described above. With these reagents, a so-called "double pipette" (Figs. 80 and 81) must be used. In this form of apparatus, the reagent in B comes into contact with an atmosphere free from oxygen, the indifferent gas being kept in place by water in the bulbs F and G.

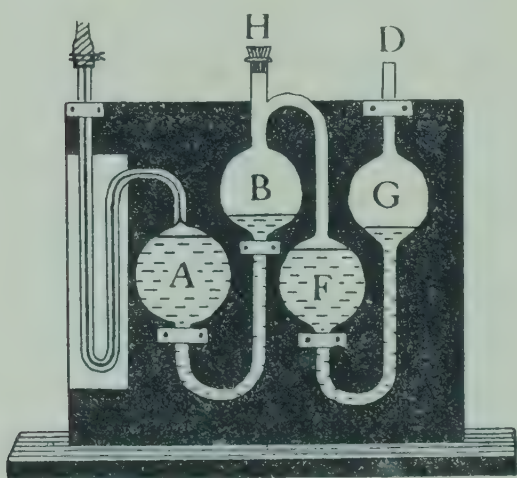


FIG. 80.

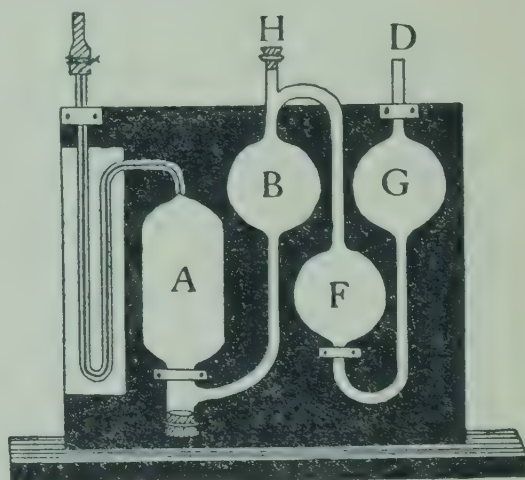


FIG. 81.

The filling of a Hempel double pipette, as ordinarily constructed, offers some difficulty. By the addition of a side-tube, shown in the diagram at H, the pipette is as easily filled as a simple pipette. The pipette is first filled with an indifferent gas, such as nitrogen or hydrogen, by passing it through while

the tube H is closed with a rubber bung. The reagent is introduced by pouring it in through the tube H, and water is poured in through D until the bulb F is almost full—in order to form a water-seal. The tube H is then closed with a well-fitting rubber stopper.

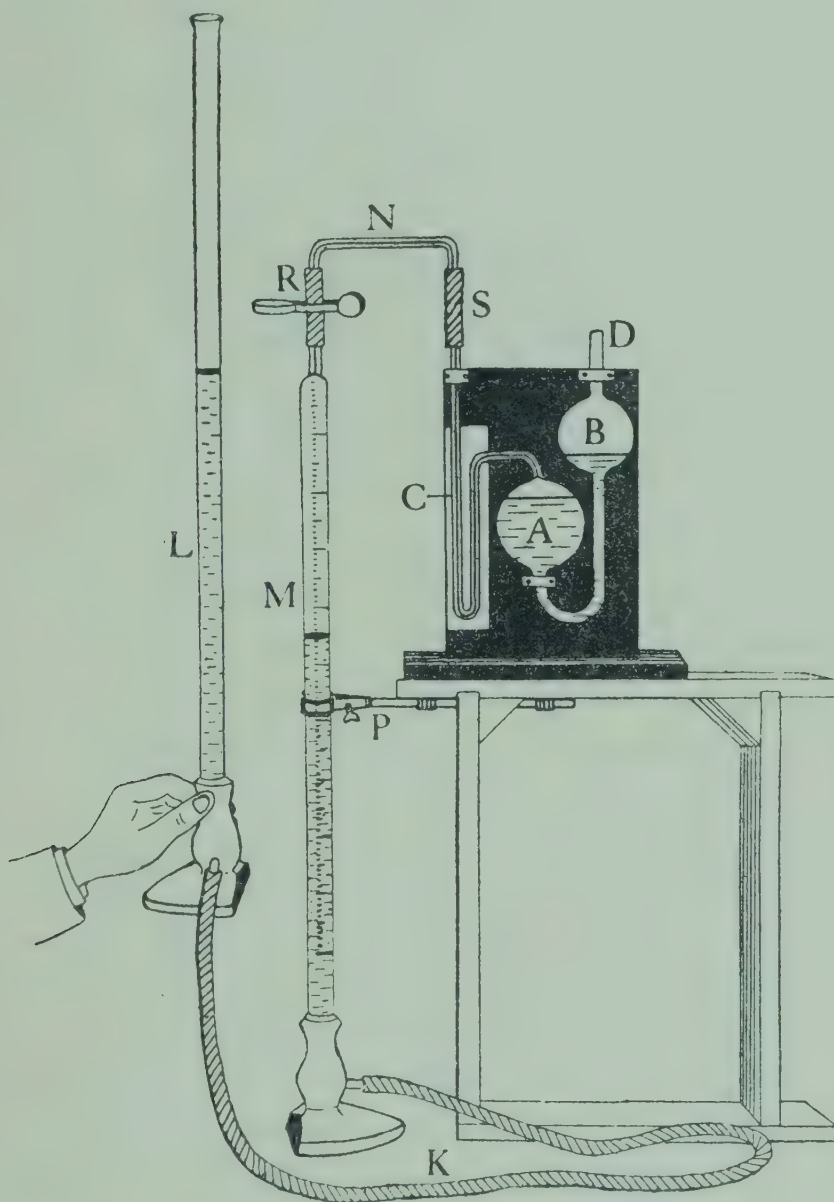


FIG. 82.

MANIPULATION OF APPARATUS

Introduce the sample of gas into the burette in the manner already described. Clamp the burette to a pipette stand as shown at P in Fig. 82. Fill the rubber tube R with water and insert the capillary tube N as close to the clip as possible. (The tube N should become filled with water.) Blow through D by means of an attached rubber tube until the capillary C and the rubber tube S become filled with liquid; then insert N and

push it down until the glass tubes touch within the rubber junction. (The capillary tubes N and C should now be almost, if not entirely, free from air; if an air column longer than 1 cm. is enclosed, the operations described above must be repeated more carefully.)

Measure the volume of the gas sample contained in the burette—say v_1 . Raise the levelling-tube, and open the clip on R *very cautiously* so that the gas enters the capillary N and drives the water over to a definite mark made on N just above the rubber tube S. Close the clip on R, equalise the levels, and read the burette again—say v_2 . (The difference between v_1 and v_2 , *i.e.* the volume of the capillary N, is usually about 0.2 ml.) Then raise L, open the clip on R, and drive the gas into the absorption pipette until water from the burette begins to flow into the bulb A by the capillary C, and close the clip on R. Bring the gas into intimate contact with the reagent by rocking the whole apparatus gently *backwards and forwards*. (This is unnecessary with a potassium hydroxide pipette containing wire gauze, or with a solid reagent such as phosphorus, on account of the large surface exposed to the gas.)

Rock the gas-pipette for five minutes, then raise L and open the clip on R so as to rinse the end of the capillary C (where it joins A) with clean water from the burette. Lower L, the clip on R being open, and bring the gas back into the burette until the reagent reaches the mark above the rubber tube S. Roughly equalise the levels, close the clip on R, and allow two minutes for the water to drain from the side of the burette. Equalise the levels and read the new volume of the gas. Repeat the operations—by passing the gas into the pipette again and back into the burette for measurement—until a constant value for the new volume (v_3) is obtained. Absorption is then complete. The final volume should not be read for five minutes, so that the temperature may become constant, and gas be resaturated with aqueous vapour. The difference between the second reading (v_2) and the last reading (v_3) gives the volume of gas absorbed; and if the original volume (v_1) of the gas was 100 ml., the difference in millilitres is the percentage of the constituent in the mixture.

In order to determine the amount of a second constituent in the mixture, the original pipette with its rubber tube S is removed, the clip on R being, of course, closed; only a very

small amount of reagent remains in the end of the tube N and serves to seal the capillary. A second pipette is then attached to N as before, and, the volume of the gas having been already measured to the mark on N, the absorption of the second constituent may be begun at once.

The final (true) volume of the residual gas may be found by adding the correction for the capillary N (usually about 0.2 ml.) to the last volume observed.

ANALYSIS OF A GASEOUS MIXTURE

In the analysis of a gaseous mixture the gases must be determined in a definite order. The order in which the reagents *must* be used is given below for a mixture of the commoner gases ; if a gas is known to be absent, the corresponding reagent will, of course, be omitted.

- I. Potassium hydroxide *for carbon dioxide.*
- II. (a) Bromine ; or (b) Fuming sulphuric acid (followed in either case by potassium hydroxide) *for ethylene, and other unsaturated hydrocarbons.*
- III. (a) Sodium dithionite ; or (b) Phosphorus ; or (c) Alkaline pyrogallate ; or (d) Chromous chloride *for oxygen.*
- IV. (a) Cuprous sulphate- β -naphthol, or (b) Ammoniacal cuprous chloride (followed by dilute sulphuric acid) *for carbon monoxide.*
- V. The unabsorbed residue is analysed as described on p. 471 *for methane, hydrogen, and nitrogen.*

REAGENTS USED IN ABSORPTION PIPETTES

Potassium Hydroxide. (*For carbon dioxide.*)—Dissolve 500 grams (or the contents of a 1-lb. bottle) in 1 litre of water and store in a bottle with a rubber stopper. Pack the absorption bulb of a simple pipette (Fig. 79) with rolls of iron wire gauze of wide mesh and fill with the solution of potassium hydroxide. When wet with this solution, the iron does not

take up any oxygen by oxidation. Absorption of carbon dioxide in this pipette is usually complete in less than a minute.

One ml. of the reagent will effectively absorb about 40 ml. of carbon dioxide.

Sodium hydroxide must not be used instead of potassium hydroxide, as sodium bicarbonate is liable to crystallise out and block the capillary tube.

Bromine. (*For ethylene and other unsaturated hydrocarbons.*)—Introduce into bulbs A and B of a double pipette (Fig. 80) the correct amount (as illustrated) of a saturated aqueous solution of bromine, and pour in a few millilitres of liquid bromine to ensure that the solution remains saturated. Pour water into F and G.

After the gas has been in contact with the reagent in the pipette for five minutes, draw it back into the burette, and then pass it into a potassium hydroxide pipette in order to remove bromine vapour; finally, return the gas to the burette, and measure it.

Fuming Sulphuric Acid. (*For ethylene and other unsaturated hydrocarbons, and benzene.*)—This reagent absorbs the same gases as bromine. A simple pipette, filled with glass

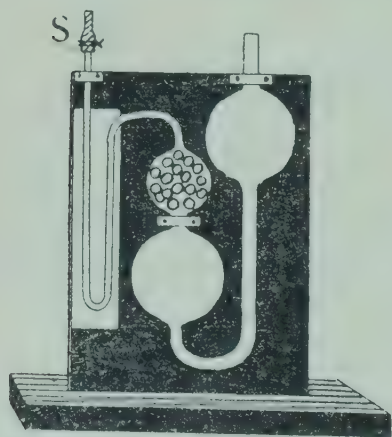


FIG. 83.

beads or rods, may be used, but the special form with three bulbs, shown in Fig. 83, is recommended. The pipette is filled as usual, but great care must be taken that the reagent does not come into contact with the rubber connections or with water. The connecting-tubes must not be filled with water, and, when the gas is transferred to the pipette, care must be taken to prevent any water passing over into the pipette. The absorption

is complete within five minutes. When the gas is withdrawn for measurement, allow the fuming sulphuric acid to follow until it reaches a mark made on the pipette capillary, showing the position of the reagent at the start of the experiment. (It is evident that an error is introduced on account of the air in the capillary. If the volume is known, a correction may be applied, but for many purposes the error is negligible; in any case the error affects only the oxygen and nitrogen determinations to any appreciable extent.) As fuming sulphuric acid has a high

vapour pressure, acid vapour must then be removed from the gas by passing it into a potassium hydroxide pipette before measurement.

The pipette must be refilled after about 1 litre of ethylene has been absorbed.

Sodium Dithionite (*For oxygen.*)—Dissolve 25 grams of sodium dithionite in 165 ml. of water and add 30 ml. of 50 per cent. sodium hydroxide. Introduce the solution at once into a double pipette. The reaction that occurs in the absorption of oxygen is represented by the equation



The absorption is complete within five minutes even at low temperatures, and is unaffected by ethylene, ammonia, etc. The addition of 3 grams of sodium anthraquinone- β -mono-sulphonate hastens the absorption of oxygen. The pipette should be refilled after about 300 ml. of oxygen have been absorbed. The dithionite solution should be freshly prepared, as it does not keep.

Phosphorus. (*For oxygen.*)—The bulb of a simple pipette (Fig. 79) is packed with thin sticks of ordinary yellow phosphorus. The pipette is previously filled with water, and the bulb is covered with a metal cover to protect the phosphorus from the action of light.

Absorption of oxygen is marked by the appearance of white clouds of the oxide, and is complete within five minutes if the temperature is above 15° ; at lower temperatures the absorption is much slower, and in cold weather sometimes does not occur at all unless the water in the pipette is warmed.

No absorption of oxygen takes place if the partial pressure of the oxygen is greater than about 0.5 atmosphere, or if the mixture contains ethylene, heavy hydrocarbons, ammonia, or alcohol, even in traces. If no white fumes appear, further treatment with bromine or fuming sulphuric acid should be carried out before oxygen is presumed absent. A mixture containing above 50 per cent. of oxygen may be diluted with a known volume of nitrogen, and the oxygen will then be absorbed.

Phosphorus is much cleaner to work with than alkaline pyrogallate, and the pipette can be used for scores of analyses. The water must be changed from time to time. An error is liable to result from the use of phosphorus in the analysis of a

gas mixture containing oxygen together with hydrogen or carbon monoxide, the latter gases being appreciably oxidised. In such cases one of the other absorbents should be used.

Alkaline Pyrogallate. (*For oxygen.*)—Dissolve separately 7 grams of pyrogallol in 25 ml. of water, and 50 grams of potassium hydroxide in 110 ml. of water. Mix the two solutions and introduce *at once* into a double pipette. Potassium hydroxide purified by alcohol must not be used.

The reagent absorbs oxygen very slowly at temperatures below 10°, but the absorption is rapid and complete at higher temperatures. The pipette must be refilled after about 200 ml. of oxygen have been absorbed, as carbon monoxide is liable to be evolved from a solution nearing exhaustion. The reagent will absorb oxygen in presence of ethylene, ammonia, and other substances that interfere with the absorption of oxygen by phosphorus; but it should not be used for nearly pure oxygen, as carbon monoxide may be given off.

Chromous Chloride. (*For oxygen.*)—Transfer about 80 grams of chromic chloride to a stoppered bottle of about 400 ml. capacity. Add about 215 ml. of water, and 32 ml. of concentrated hydrochloric acid. Shake the contents of the bottle until the chromic chloride has dissolved. Add 300 grams of zinc amalgam (see p. 141), and shake vigorously until the solution becomes blue in colour, indicating that most of the chromic chloride has been reduced to the chromous state. The solution must be used in a double pipette.

Cuprous Sulphate- β -Naphthol. (*For carbon monoxide.*)—Cautiously add 200 ml. of concentrated sulphuric acid to 25 ml. of water and cool the mixture. Grind 20 grams of cuprous oxide with the acid in a mortar, adding later 25 grams of β -naphthol, until most of the solid has disappeared. Filter through glass wool, and transfer to a Hempel pipette. (The cuprous oxide is prepared by dissolving 100 grams of copper acetate in a litre of water, heating to boiling, and adding a solution of 60 grams of glucose and 50 grams of sodium hydroxide in 400 ml. of water. The liquid is boiled for a few minutes and filtered through a Büchner funnel. The precipitate is washed with water and alcohol or acetone, and dried.)

This reagent, though rather slow in action, is better than cuprous chloride in ammonia, as it absorbs carbon monoxide completely, and does not absorb either hydrogen or methane

as cuprous chloride is stated to do. The reagent will absorb more than five times its volume of carbon monoxide. Since traces of acid gases are liable to be produced, it is advisable to pass the gas into the potassium hydroxide pipette before final measurement.

Ammoniacal Cuprous Chloride. (*For carbon monoxide.*)

—Dissolve 15 grams of cuprous chloride and 10 grams of ammonium chloride in the minimum quantity of concentrated ammonia solution, and dilute to 200 ml. Transfer the solution at once to a double pipette filled with rolls of copper gauze.

This reagent is used for the absorption of carbon monoxide, but, as it also absorbs carbon dioxide, oxygen, and ethylene, these gases must have been previously removed. Carbon monoxide forms with the reagent a compound having an appreciable dissociation pressure, and it is therefore necessary to pass the gas through two pipettes; the first may contain reagent that has been used several times, but the reagent in the second pipette should be as fresh as possible. The gas and the reagent *must* be brought into intimate contact by being shaken (see below). Before measuring, the gas must be passed into a pipette filled with dilute sulphuric acid in order to remove the ammonia that escapes from the reagent.

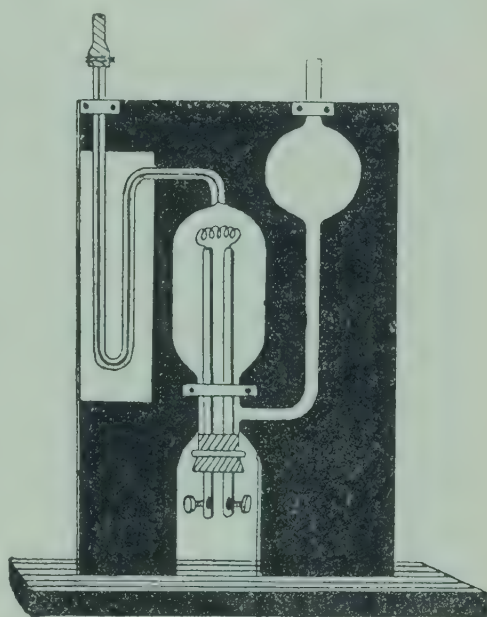


FIG. 84.

**Analysis of a Mixture of Methane,
Hydrogen, and Nitrogen**

OUTLINE OF METHOD.—After removal of all other gases, the methane and hydrogen are burned in a measured volume of oxygen. The products of combustion are removed, the contraction in volume is noted, and the amount of unused oxygen is determined. From the data obtained, the amounts of methane and hydrogen can be calculated. The residue is nitrogen.

Procedure.—Other gases are removed in the usual manner. The residue of methane, hydrogen, and nitrogen is transferred to a slow-combustion pipette (Fig. 84) in which the methane

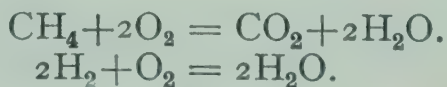
and hydrogen are burned by admitting a slow stream of oxygen, the necessary heat being supplied by an electrically heated platinum spiral. The spiral, which should be situated about 1 cm. from the top of the bulb, is heated to *dull redness* by means of a current from a 4- or 6-volt accumulator. An adjustable resistance is required for regulating the current.

Pass the gas into the pipette and see that the capillary is completely filled with water. Close the rubber tube on the pipette with a screw-clip, disconnect from the burette, and connect with a second burette containing exactly 100 ml. of oxygen.¹

After starting the heating current, raise the levelling-tube, place it on a tall stand, and open the screw-clip cautiously so that oxygen is driven *very slowly* into the pipette—at the rate of about 5 ml. per minute. (If the oxygen enters more rapidly, an explosion may occur.) During the combustion the spiral glows more brightly and the current must be regulated so that the wire is not heated much above dull redness. While combustion is in progress, the volume of gas in the pipette will decrease; when combustion is complete the volume will steadily increase. After a decided excess of oxygen has been added, close the clip on the pipette and continue to heat the spiral for two or three minutes.

Pass the gas back into the original burette, and then, without previous measurement, into a potassium hydroxide pipette, in order to remove the carbon dioxide formed by the combustion of the methane. Return the gas to the burette and measure the volume. Absorb the excess of oxygen with phosphorus or sodium dithionite, and measure the residue.

The reactions that occur in the combustion are—



If x be the volume of methane in the mixture, the volume of oxygen required for its combustion is $2x$; and if y be the volume of hydrogen, the volume of oxygen required for its combustion is $\frac{y}{2}$.

¹ For the preparation of pure oxygen, see Appendix, p. 516. For this experiment, the oxygen is collected in a gas-holder and stored till required. It should be analysed, and a correction applied if it contains any nitrogen.

After combustion, the water and carbon dioxide are absorbed by the reagents. The contraction in volume resulting from the combustion of methane is three times the volume of the methane, *i.e.*, $3x$; and the contraction resulting from the combustion of hydrogen is one and a half times the volume of the hydrogen, *i.e.*, $\frac{3y}{2}$.

We have therefore :—

$$(1) \text{ The volume of oxygen used in the combustion} = 2x + \frac{y}{2}.$$

$$(2) \text{ The contraction in volume on combustion} = 3x + \frac{3y}{2}.$$

From these two equations the quantities of methane and hydrogen are calculated.

The final unabsorbed residue is nitrogen, which, after correction for any nitrogen introduced with the oxygen, gives the quantity of nitrogen in the original mixture. This volume is, of course, the same as that obtained by subtracting the total of all the other constituents from the original volume.

There is no simple method for the direct determination of nitrogen.

Gas Analysis with the Ambler Portable Apparatus

The Ambler apparatus¹ is made in two forms, one for precision and the other for technical work. Using the latter variety, the analysis can only be carried out at constant pressure as in the Hempel apparatus, but in the precision type

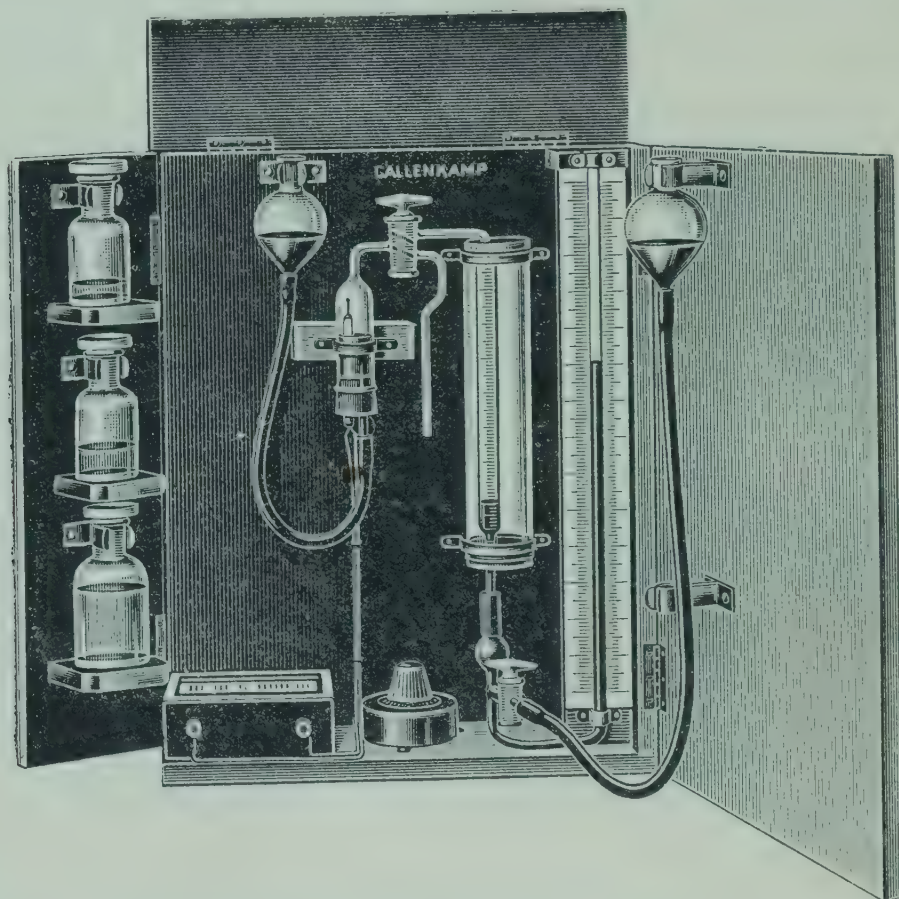


FIG. 85.—Ambler's Portable Apparatus for Accurate Gas Analysis.

measurement can be made of the volume, pressure or both. Measurement at constant volume gives the most accurate results, but it is in some cases more convenient to keep the pressure approximately constant and measure both pressure and volume. Laboratory patterns of Ambler's apparatus have been designed for precision work on samples down to 1 ml. Only the portable types are described below.

The absorption pipette A (Fig. 86) is permanently attached to the burette B which is kept at approximately constant temperature by a water jacket. Thus leakage which might occur through a rubber joint is avoided. Other advantages

¹ This apparatus is supplied by A. Gallencamp & Co. Ltd., London.

of the apparatus over the Hempel type are the elimination of loss by dissolution of gases in the confining liquid as this is mercury, and the negligible loss by physical dissolution in the absorbent reagents since only about 2 ml. of each is required. The reservoirs R_1 and R_2 which can be moved to any required position or supported in suitably placed clips enable the gas

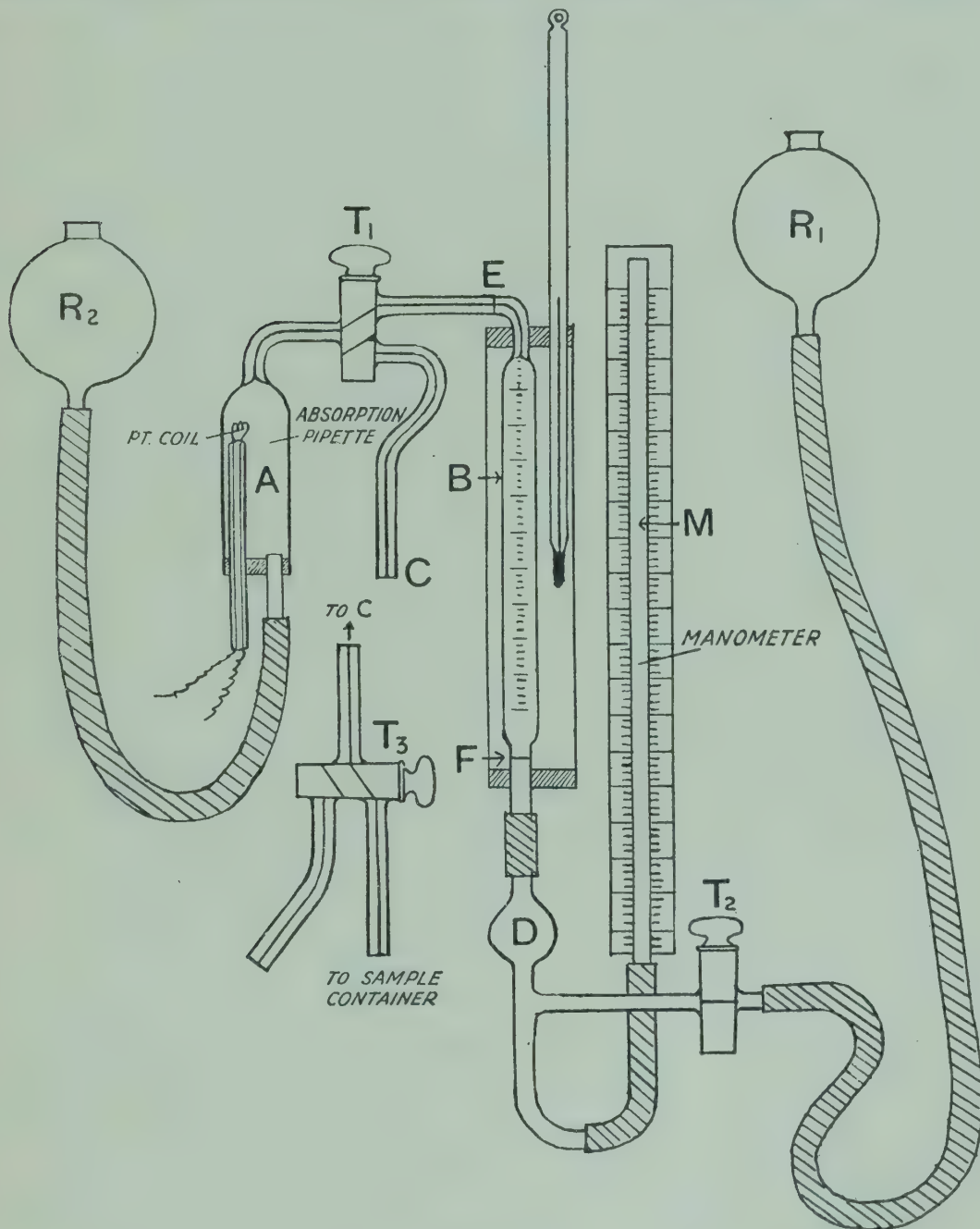


FIG. 86.

to be transferred from the absorption pipette to the burette or *vice versa*. R_2 is used also to draw in the sample and the various reagents through C, by manipulation of the two-way tap T_1 . The pressure in the burette is measured by means of the manometer M, and the tap T_2 is used for accurate control of the flow of mercury to and from R_1 . The capillary tube is

marked at E between the tap T_1 and the burette, and the graduations on the burette give the volume of the space above the mercury level plus the volume of the capillary tube to the mark E. Another mark is placed at F on the narrow tube below the burette for use when the constant volume method is employed, greater accuracy being thus attained than would be the case using some point on the wider burette tube.

After absorption by the usual reagents, the residual gases are mixed with air and gradually burnt in A by means of a heated platinum spiral connected to leads from a battery.

Although the volume of the gas sample taken for analysis is only about 10 ml., measurements can be made with an error of only 0.1 per cent. in the precision apparatus and about 0.5 per cent. in the technical model. Since mercury is used in this apparatus, in the Lunge nitrometer, and in the Haldane apparatus, some precautions which should be taken may be noted here. Mercury vapour is highly poisonous and although its vapour pressure at ordinary temperatures is very small, it may produce ill effects if spilt on the bench and floor, especially in badly ventilated rooms. This arises from the large total surface of innumerable small drops and the cumulative effect of the poison. If mercury is to be dried by heating, this should always be done in a fume chamber with a good draught. In order to minimise the risk of the metal being spilt on the bench or floor, all apparatus involving its use should be placed on non-metallic trays or drawers with well-fitted low sides.

It is not possible to make accurate measurements with impure mercury as it is apt to stick to the sides of the measuring vessel. A rapid and convenient treatment which results in a sufficiently pure metal for use in gas analysis consists of shaking it with a solution of mercurous nitrate containing some nitric acid. By this treatment dissolved metals which are electropositive to mercury go into solution displacing mercury from the mercurous nitrate. Pour the mercury into a stoppered bottle of about twice the volume of the metal to be purified, and for each 100 ml. add about 20 ml. of dilute nitric acid, 20 ml. of water and 10 grams of mercurous nitrate. Secure the stopper firmly and shake the bottle vigorously for at least five minutes. Pour off the aqueous layer into a large beaker (to avoid any mercury getting into the sink) and wash the mercury by shaking it with six successive lots of about half its

volume of water, pouring each lot into the beaker. Finally, pour the mercury into an evaporating dish and dry it as far as possible with filter paper, and then by heating the dish over a small flame in a fume chamber so that a thermometer suspended in the liquid shows a temperature between 105° and 110° .

After the mercury has cooled completely, pour it into a funnel fitted with a filter paper which has been pierced with a pin near the apex of the single fold, and collect the mercury in a clean bottle. The filter paper retains any mechanical impurities floating on the surface of the mercury.

If it is desired to calibrate the burette, remove the key of T_1 and lower R_1 to remove mercury from the burette and the bulb D. Close T_2 and disconnect D from the burette. Attach one tube of a short capillary tap to the burette and the other to the rubber tube of an auxiliary mercury reservoir. Fill the burette with mercury exactly up to the mark E, making sure that no air is trapped above the tap. Pour the mercury out of the reservoir and disconnect it from the tap without shaking any mercury out of the latter. Place a tared weighing bottle below the tap and very carefully run out mercury until the meniscus is exactly on the first graduation to be tested. This can be more accurately attained by holding a small piece of mirror behind the burette. The highest part of the mercury meniscus should be in line with the reflection of the centre of the eye. Close the tap and weigh the weighing bottle and mercury. Replace the weighing bottle under the tap and run out mercury to the next point to be tested and so on down to the 10 ml. mark. In special cases it is useful to know the volume between the mark F and the 10 ml. mark. Calculate the volumes of the various points tested, using the following table :—

Temperature.	Volume in ml. of 1 gram of Hg.	Temperature.	Volume in ml. of 1 gram of Hg.
5°	0.07362	20°	0.07382
10°	0.07369	25°	0.07389
15°	0.07375	30°	0.07395

Before the practical details of the analysis are described, the three different methods of measuring the gas will be considered.

(1) *Measurement of Volume at Constant Pressure.*—In this method the mercury in R_1 (Fig. 86) is brought as nearly as possible to the same level as the mercury in the burette, and the volume of the gas is then read. It is the simplest procedure of the three methods and suitable for gas of any composition. Because of the difficulty in placing the mercury in R_1 exactly level with that in the burette and the considerable diameter of the burette, the average error in measurement of the volume is about 0.5 per cent. by this method, but this is permissible in technical work.

(2) *Measurement of Pressure at Constant Volume.*—By this method the error of measurement is reduced to about 0.1 per cent. because the gas is confined between the mark E above the burette and the mark F below it, both of these marks being on narrow tubes, and the pressure is read on the narrow manometer tube M. Before the composition of the gases can be calculated, the reading on the manometer must be determined when the burette is filled to the mark F with air at atmospheric pressure. This is done by temporarily removing the key of T_1 , placing R_1 so that the mercury is exactly at the mark F, closing T_2 , and reading the manometer.

Let this reading be M_1 , and let M_2 be the reading on the manometer when the burette is filled to the mark F with the gas to be analysed. If the atmospheric pressure is B , the pressure of the gas in the burette will be $B + M_2 - M_1$, but since the burette is washed out with water before the analysis, a deduction must be made for the vapour pressure of water at the temperature of the burette. Let this be W . The pressure of the gas is therefore $B + M_2 - M_1 - W$ mm. If the volume of the burette down to the mark F is V ml., the volume the gas would occupy at 760 mm. pressure would be $V \frac{(B + M_2 - M_1 - W)}{760}$ ml., and if after absorption of one of the constituents, the manometer reading is M_3 , the volume of that constituent will be $V \frac{(M_2 - M_3)}{760}$ ml., and its percentage will be

$$V \frac{(M_2 - M_3)}{760} \cdot \frac{760}{V(B + M_2 - M_1 - W)} \cdot 100 = \frac{(M_2 - M_3)}{(B + M_2 - M_1 - W)} \cdot 100.$$

Thus the volume V need not be known, and the percentage of each constituent is proportional to the difference between

successive manometer readings, $(B + M_2 - M_1 - W)$ being a constant for the particular conditions of the analysis.

If it is found that after several absorptions or after combustion a diminution in volume of more than 20 per cent. has occurred, it may not be possible to bring the mercury level to the mark F. The same method can still be applied, though with less accuracy, by repeating the analysis, but this time setting the mercury level initially at the 10 ml. mark. After one or more absorptions have taken place the mercury is set at some point higher up the burette, say at the 7 ml. mark. Then if p_1 = the initial pressure at the 10 ml. mark, and p_2 = the pressure after absorption with mercury at the 7 ml. mark, the percentage of the constituent absorbed

$$= \left[\frac{p_1 - \frac{7}{10} p_2}{p_1} \right] 100.$$

Repetition of the analysis can be avoided if the volume between the mark F and the 10 ml. mark is known. If this volume = x , p_2 in the above equation must be multiplied by $\frac{7}{10+x}$ instead of $\frac{7}{10}$.

(3) *Measurement of Volume at approximately Constant Pressure.*—In this method the mercury in R_1 is brought to within about 2 mm. of the level of that in the burette. T_2 is then closed, and the meniscus is read in the burette and in the manometer. The volume of the gas at exactly atmospheric pressure is then calculated. In order to do this, a series of readings is made of the mercury meniscus in the burette and manometer at atmospheric pressure, say, at the 3 ml., 5 ml., 7 ml., and 9 ml. marks on the burette. Readings are made with the key of T_1 removed, and a curve of the results is plotted.

The gas pressure in the burette can be expressed as $B - W \pm dp$ where B = the atmospheric pressure, W = the vapour pressure of water at the temperature of the burette, and dp is the difference between the reading on the manometer with the gas at approximately atmospheric pressure and that obtained from the curve giving the manometer reading corresponding to the volume reading on the burette at atmospheric pressure.

The volume the gas would occupy at atmospheric pressure is therefore

$$V_a = V \frac{(B-W \pm dp)}{B-W}$$

or

$$V_a - V = \pm \frac{V dp}{B-W}$$

and this is the actual correction to be applied. If, for example, dp is ± 2 mm. and $B-W$ is $760-10$ mm. and $V = 10$ ml.,

$$V_a - V = \pm \frac{10 \times 2}{750} = \pm 0.0267 \text{ ml. or } \pm 0.27 \text{ per cent. of } V.$$

Ordinary variations in the atmospheric pressure will not introduce an error of more than about 0.02 per cent. on the total volume if dp is not greater than about 2 mm.

Procedure for the Analysis of the Gas

The best method of introducing the sample will depend on the available supply of the gas, but it is in any case advisable to attach the common tube of an auxiliary two-way capillary tap T_3 to the tube C by a short piece of pressure tubing. By raising R_2 and turning T_1 , mercury is driven up to the left-hand side of T_1 which is then closed. One of the other tubes of the tap T_3 is connected to the source of the gas, and if this is available in quantity as *e.g.* flue gas, some is drawn into A by lowering R_2 and turning T_1 . It is then expelled through the free end of T_3 and this process repeated several times. The absorption vessel A is then nearly filled with the gas which should now be free from air. If the supply is limited as in the case of a sample in a tube closed by two taps, one of these is connected to the auxiliary tap T_3 and a little of the sample is drawn into the top of A. It is then expelled through the free tube of T_3 , and followed up with mercury until the capillaries as far as T_3 are filled with mercury. R_2 is lowered as far as possible and the gas drawn into A. If this is insufficient for the analysis it can be transferred to the burette and more gas withdrawn from the sample tube, which will then be at a pressure considerably below that of the atmosphere.

For Method 1, in which the volume is measured at constant pressure, a total volume of about 9 ml. of gas at atmospheric pressure should be transferred to B. After T_1 has been closed,

R_1 is held so that the mercury in it is as nearly as possible level with that in B. The volume of the gas is read after T_2 has been closed.

If the pressure at constant volume is to be measured as in Method 2, open T_1 and lower R_1 sufficiently to bring the mercury meniscus into the bulb below the burette, so that when T_1 is closed and the mercury brought exactly to the mark F by raising R_1 , the gas will be under a pressure of about 250 mm. above atmospheric pressure. The mercury in the manometer should therefore be about 250 mm. above the mark F. The best way to bring the mercury exactly to the mark F is to close T_2 , support R_1 in the upper clip provided, and very gradually turn T_2 , allowing mercury to flow slowly to the mark, and then close it again. Care must be taken to see that mercury is not driven out of the top of the manometer tube if R_1 has to be raised above the apparatus. The pressure is not read until the excess of the gas sample in A has been discharged (see below).

In the third method in which both volume and pressure are measured the initial volume of gas taken should be between 9 and 10 ml. with the mercury in R_1 placed within ± 2 mm. of the mercury level in the burette. After T_2 has been closed, the burette and manometer readings are taken. It is necessary to close T_1 before making any gas measurements in the burette.

After each absorption in the analysis, measurement of the remaining gas is carried out as above according to which method of measurement is adopted. Whichever method is used the excess of the gas sample in A is expelled through the tube C which is left full of mercury, any of the metal discharged from C being collected in a small beaker. Then in the case of Method 2 *only*, before the pressure on the manometer is read, T_1 is reversed and mercury is driven past the tap to the mark E, and this procedure is adopted in subsequent measurements during the analysis using this method. The reason for doing this is to guard against possible gas leaks past T_1 when the pressure is above atmospheric. Working at constant pressure, it is more convenient not to allow the mercury in A to go beyond the left-hand side of T_1 when transferring gas to the burette. Though the burette is calibrated to hold the nominal volumes from the mark E, the error introduced by leaving gas in the capillary from E to the left-hand side of T_1 is only

about 0.02 ml., and for the constant pressure method may usually be neglected.

Absorption of the gases is carried out in the same order as in the Hempel apparatus, carbon dioxide being first removed by potassium hydroxide. Not more than 2 ml. of this reagent (see below) is drawn into A through C which has been filled with mercury. If any air bubble is seen in A it must be expelled through C. The gas is driven over from the burette, and the apparatus gently shaken to hasten the absorption. Except in the case of absorption of carbon dioxide which is rapid, the shaking should be continued for two or three minutes. Drive the gas back into the burette, but do not let the reagent floating on the mercury go beyond the left-hand side of T_1 at this stage even when measuring at constant volume. After measuring the gas, drive it back into A for further treatment with the potassium hydroxide to make sure that absorption is complete. Return the gas to the burette, and when the reagent has reached the left-hand side of T_1 , close T_1 . If no further absorption appears to have taken place, expel the reagent through C into a small beaker and discard it. If the measurement is being made at constant volume, carefully bring the mercury along to the mark E, before finally reading the pressure. As stated before, these adjustments are best made by careful control of T_2 .

If unsaturated hydrocarbons are present they are absorbed next, but in the case of benzene and its homologues it is advisable to absorb these before determining carbon dioxide, as they are appreciably soluble in aqueous solutions. Fuming sulphuric acid (oleum) must be used in this apparatus because bromine is precluded on account of its action on mercury. The oleum should contain not less than 10 per cent. free sulphur trioxide and not much over 20 per cent., as acid that contains more may solidify at low temperatures. In order to prevent generation of excessive heat, care must be taken in drawing oleum into A. Any alkali left in A must first be washed out with dilute sulphuric acid, and this followed by about 1 ml. of a cooled mixture of 3 ml. of concentrated sulphuric acid and 1 ml. of water. After this has been expelled and C filled with mercury, about 2 ml. of oleum are drawn into A. The gas is transferred to A and the apparatus gently shaken for several minutes to make sure of complete absorption so as to avoid the

necessity of a second treatment with this reagent if possible. The gas is transferred to the burette, the oleum expelled through C, and A is washed successively with the 3 to 1 acid mixture, dilute sulphuric acid, and finally potassium hydroxide reagent. Before the alkali is expelled from A the gas is driven into A, and the apparatus is shaken to remove acid fumes from the gas, which is then returned to the burette for measurement.

If the temperature is above 15° , oxygen may be absorbed by alkaline pyrogallol solution. This is done by first drawing in about 2 ml. of the potassium hydroxide solution used for absorption of carbon dioxide, wiping the end of tube C to avoid contamination of the stock pyrogallol solution, and introducing about 0.5 ml. of pyrogallol solution. For temperatures below 15° it is better to use sodium dithionite solution containing a little sodium anthraquinone- β -monosulphonate. The absorption of carbon monoxide by ammoniacal cuprous chloride should be carried out in three stages, using each time about 1 ml. of the solution prepared as described below. This procedure is advisable because of the appreciable dissociation pressure of carbon monoxide from a solution of the reagent which has absorbed some of the gas. After it has been washed with 1 ml. of water to remove ammonia, the remaining gas is measured in the burette. The following reagents are used :—

1. *Potassium Hydroxide (for Carbon Dioxide)*.—Dissolve 24 grams in 36 ml. of water.

2. *Pyrogallol Solution (for Oxygen)*.—Dissolve 12 grams in 36 ml. of water. This is not mixed with alkali until it is drawn into A.

3. *Sodium Dithionite (for Oxygen)*.—Prepare this as required by dissolving 1.6 gram of sodium dithionite in 10 ml. of 2N sodium hydroxide, and transfer it to a very small bottle to avoid contact with air. The addition of 0.2 gram of sodium anthraquinone- β -monosulphonate hastens the absorption of oxygen and shows a colour change from red to brown when the solution is exhausted.

4. *Ammoniacal Cuprous Chloride (for Carbon Monoxide)*.—Dissolve 3 grams of cuprous chloride and 2 grams of ammonium chloride in the minimum volume of concentrated ammonia, and dilute to 40 ml.

Combustion of Hydrogen and Methane

After the gases already considered have been absorbed, hydrogen and methane if present can be determined by slow combustion in the residual gas. To avoid risk of an explosion, the hydrogen after mixing with excess of air should not constitute more than about 10 per cent. of the mixture. For methane the limit is about 6 per cent., and if both of these gases are present the limit for the total combustible gas will be some intermediate value. By adjusting the amount of air so that there is less than 3 per cent. of hydrogen in the gas ready for combustion, it is possible to burn it alone leaving the methane unaffected. For this purpose the platinum spiral is kept at a dull red heat just visible in daylight against a dark background. Only about one minute is required for burning the hydrogen, but the electrical heating, which is controlled by a rheostat, must be applied very gradually to avoid burning some of the methane in the first few seconds. After measurement of the contraction the gas is returned to A, and the platinum spiral is heated to a bright yellow colour for two minutes in order to burn the methane. The carbon dioxide formed is absorbed by drawing into A about 2 ml. of potassium hydroxide reagent before measuring the remaining gas.

Since the hydrogen in the gas mixture for this fractional combustion must not exceed 3 per cent., the necessary oxygen if not already present is conveniently added in the form of air. If the composition of the gases which are not absorbable is quite unknown, or if they are believed to contain too high a percentage of hydrogen, a trial should be made with, say, a third of these residual gases, the excess being discharged through C and collected over mercury in case it should be required for a determination using a larger proportion. The measurements to be made, therefore, in this fractional combustion method are the volumes :—(1) of the total residual gas ; (2) of the residual gas used if only part is taken ; (3) after addition of excess of air ; (4) after combustion of the hydrogen and cooling ; and (5) after combustion of the methane and absorption of carbon dioxide. Since the contraction on burning the hydrogen is one-and-a-half times its volume, and in the case of methane is three times its volume after absorption of the carbon dioxide (see p. 473), the percentage change on com-

bustion must be divided by 1.5 in the case of hydrogen, and by 3 in the case of methane.

As an alternative to the fractional combustion, hydrogen and methane, if both are present, can be burnt at the same time and their percentages determined by measurement of the carbon dioxide formed, and the total contraction (or diminution of pressure) after absorbing the carbon dioxide. The carbon dioxide formed will be equal to the volume of methane producing it, and the contraction from the hydrogen combustion will be equal to the total contraction (after absorption of carbon dioxide) less that from the combustion of the methane.

The apparatus can be conveniently used for the determination of oxygen even in very low percentages, because burning the oxygen with excess of hydrogen causes a contraction that is three times the volume of the oxygen; an additional advantage is the cleanliness of the determination.

The following general precautions must be observed in using the apparatus. The absorption pipette and burette must be washed out with dilute sulphuric acid at the end of an analysis, as alkali left in contact with the accurately ground surfaces of the tap T_1 is very injurious. This tap should be kept lubricated with the minimum quantity of a good tap grease. If carbon dioxide resulting from combustion is to be determined, the apparatus must be washed free of alkali before combustion is carried out. To do this the gas is transferred to the burette and A is washed out once with dilute acid and twice with water. About 1 ml. of water is transferred to the burette, T_1 is closed, and R_1 lowered so as to wash the lower part of the burette also. The gas and water are then driven into A, and after the gas has been returned to the burette the water is expelled through C. If any reagent accidentally enters the burette it must be washed out at once, because the gas should always be measured when saturated with water vapour.

The Haldane Apparatus

For the analysis of air in mines, the Haldane apparatus is commonly employed. Mercury is used as the confining liquid, and thus any error from solubility of carbon dioxide or other gases is eliminated. The burette consists of a wide top portion, joined to a graduated tube of narrow bore at the bottom which

enables very small alterations in volume of the gas to be observed accurately. This is essential in determining the percentage of carbon dioxide in air by an absorption method. A slow-combustion pipette is included in the apparatus by means of which carbon monoxide, hydrogen, and methane can be determined.

Analyses Involving the Use of a Lunge Nitrometer

THE Lunge nitrometer (Fig. 87) consists of two glass tubes connected by a stout rubber tube. The levelling-tube L is ungraduated and is open to the air; the measuring-tube M is graduated and is fitted at the top with a three-way tap, so that the measuring-tube may be connected with either the cup C or the tube A. By means of this tap a sample of gas may be drawn into the apparatus through the tube A, and then, by turning the tap, any desired reagent may be run in from the cup C. The pressure tubing used to connect the two glass tubes should be a little longer than the measuring-tube, and must be securely wired on to the tubes.

At all times the apparatus should stand on a mercury tray. Special clamps with wide grips may be obtained for holding the apparatus, but *good* burette clamps, with rubber pads on the grips, are quite satisfactory. Each tube, when filled with mercury, weighs about 3 lb., and the use of a flimsy burette clamp means the almost certain breakage of the apparatus.

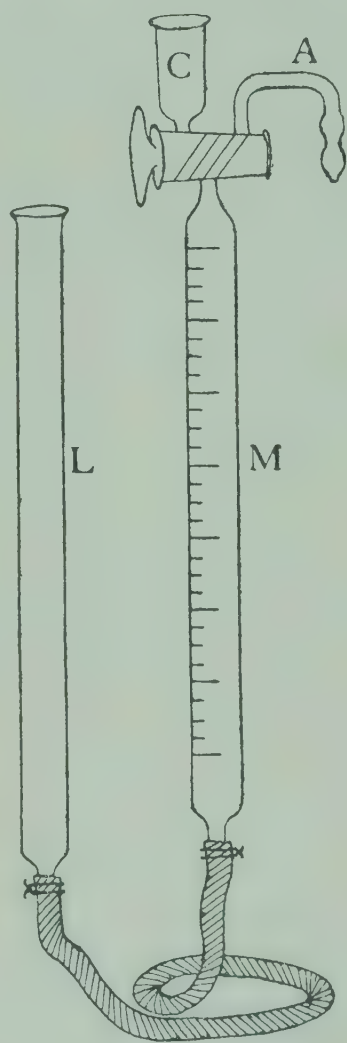


FIG. 87.

Nitrogen in a Nitrate or Nitrite

OUTLINE OF METHOD.—The nitrate or nitrite is reduced to nitric oxide by shaking with mercury and concentrated sulphuric acid in the measuring-tube of a Lunge nitrometer. The nitric oxide is measured, and, from the volume of nitric oxide, the weight of nitrogen is calculated.

Procedure.—The solution containing the nitrate should not exceed 2 ml. in volume; if necessary, it must be evaporated until reduced to this volume.

Fill the measuring-tube of the nitrometer with mercury by raising the levelling-tube. Pour the nitrate solution into the cup C. By cautiously opening the tap, run the solution into the nitrometer without admission of any air. Wash out the vessel that contained the nitrate *with a few drops* of dilute sulphuric acid, and run this in through the cup in a similar manner. (Keep the volume of liquid and washings as small as possible—the total should not in any case exceed 4 ml.) Pour about 15 ml. of concentrated sulphuric acid into the cup and run this into the nitrometer, care being taken that no air is admitted. Remove the measuring-tube from the clamp and shake with a rotary motion, so that globules of mercury are thrown up into the liquid. In a minute or two the evolution of nitric oxide will begin. If no gas appears after shaking vigorously for two to three minutes, cautiously run in a few drops of water and shake again. The shaking must be continued until the evolution of nitric oxide ceases. Allow the apparatus to assume the room temperature, and then measure the volume of the gas under atmospheric pressure.

In order to adjust the pressure, assume the density of the aqueous liquid to be one-eighth that of mercury, and clamp the levelling-tube in the appropriate position. If the adjustment is correct, it will be found that a drop of liquid in the nitrometer cup is neither drawn in nor forced out when the tap is *very cautiously* opened. Care must be taken not to warm the gas by handling the measuring-tube.

The temperature and the barometric pressure must be noted and the observed volume reduced to N.T.P. One ml. of nitric oxide at 0° and 760 mm. weighs 0.001340 gram, and corresponds to 0.000626 gram of nitrogen.

At the conclusion of an experiment, the measuring-tube may be readily cleaned by disconnecting and rinsing it three times with concentrated sulphuric acid, using 5 ml. each time.

Exercise.—Determine the percentage of nitrogen in potassium nitrate. Use about 0.2 gram.

Nitrite

When a nitrite is added to an acid solution of thiourea, the reaction that follows depends on the strength of the acid. In

presence of a weak acid, such as acetic acid, the chemical change takes place almost entirely in accordance with the equation :



whilst if hydrochloric acid is present, the interaction may be represented by the following equation :



In the first case, a little nitric oxide is always obtained, and in the second case a little nitrogen, but this does not affect the determination since the volume of gas obtained is the same in both cases. On account of the lower solubility of nitrogen, it is preferable to use acetic acid.

Procedure.—Weigh accurately about 0.15 gram of sodium nitrite. Introduce the weighed sample, together with about 0.2 gram of thiourea, into the cup of the nitrometer, and dissolve in 1 to 2 ml. of water. Run the solution into the measuring-tube and rinse the cup with *a few drops* of water. Then introduce 1 ml. of 50 per cent. acetic acid, and shake vigorously.

Gas is evolved immediately the solution is acidified, and the reaction is complete in a few minutes. In adjusting the levels, assume the density of the aqueous column to be one-thirteenth that of mercury. If the total volume of aqueous liquid is not greater than 4 ml., the error from the solubility of the gas in water is negligible.

Hydrogen Peroxide

Hydrogen peroxide, in presence of sulphuric acid, interacts with potassium permanganate as follows :—



The concentration of a solution of hydrogen peroxide may therefore be determined by measuring the volume of oxygen obtained from a known volume of the peroxide solution treatment with excess of permanganate.

The apparatus (Fig. 88) consists of a reaction together with a Lunge nitrometer. The reaction vessel of a small conical flask with a well-fitting rubber stopper which carries a glass tube. Connection with the nitrometer is made by means of a piece of glass tubing. A short wide test-tube is also required ; this

longer than the base of the flask in order that, when placed in the flask, it will remain in the position shown in the diagram.

Procedure.—Place 20 ml. of saturated potassium permanganate solution and 20 ml. of dilute sulphuric acid in the conical flask. Dilute 10 ml. of commercial hydrogen peroxide to

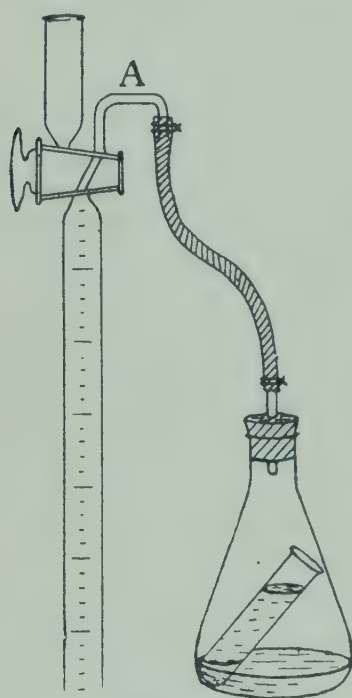


FIG. 88.

100 ml., and place 10 ml. of this diluted solution in the test-tube. Place the test-tube carefully in the flask, care being taken that no mixing of the peroxide and permanganate occurs at this stage. Insert the rubber stopper and connect the flask with the nitrometer, which is filled with mercury. Loosen the tap of the nitrometer in its socket, and place the conical flask, up to the neck, in water at the room temperature. After about five minutes, adjust the mercury to the zero mark, insert the tap firmly into position, and turn it so that the reaction vessel is connected to the measuring-tube. If the mercury level alters in the course of a few minutes, the tempera-

ture is not yet constant.

When the temperature has become constant, tilt the reaction flask so that the peroxide solution mixes with the permanganate. Keep the pressure approximately equal to the atmospheric pressure by lowering the levelling-tube from time to time. Rinse out the small tube with some of the permanganate solution by appropriate manipulation of the flask. When the reaction is apparently complete, shake the flask carefully. (The liquid, unless agitated, may retain several millilitres of dissolved oxygen.)

Adjust the mercury levels and read the volume of oxygen. Reduce the volume to N.T.P. and calculate the weight of hydrogen peroxide per litre of the original solution.

The concentration of hydrogen peroxide is commonly expressed in terms of the volume of oxygen obtained from it by decomposition by heat. Thus "10-volume" hydrogen peroxide yields ten times its own volume of oxygen at standard temperature. (It may be pointed out that double this volume of oxygen is obtained when the peroxide is treated

with permanganate.) Calculate the concentration of the peroxide solution in this way also.

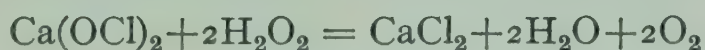
Evaluation of Zinc Dust

Zinc dust is frequently used as a reducing agent, and an estimate of its value for this purpose may be obtained by measuring the volume of hydrogen evolved when a weighed sample is treated with excess of acid.

Place about 0.1 gram (accurately weighed) of the sample in the conical flask (Fig. 88) and add 25 ml. of water. In the small test-tube place 5 ml. of concentrated sulphuric acid. Proceed as described in the determination of hydrogen peroxide. From the volume of hydrogen evolved, calculate the percentage of zinc in the zinc dust.

Available Chlorine in Bleaching-Powder

Bleaching - powder and hydrogen peroxide interact as follows :—



One ml. of oxygen at N.T.P. is equivalent to 0.00317 gram of available chlorine.

Measure into the conical flask (Fig. 88) 25 ml. of a solution of the bleaching-powder prepared as described on p. 167. In the small test-tube place 3 ml. of "10-volume" hydrogen peroxide. Proceed as described on p. 490. From the volume of oxygen evolved, calculate the percentage of available chlorine in the bleaching-powder.

Flow
ana'

Determination of Gases present only in Traces

METHODS depending on the alteration in volume produced by absorption are not suitable for the determination of traces of gases. An accuracy of 1 in 1000 in the measurement of a gas-volume is within the limits of what one would ordinarily regard as "permissible error." An illustration will make it clear that this error is far too large for many purposes. The amount of carbon dioxide in the atmosphere is usually about 3 parts in 10,000 or 0.03 per cent., and 0.03 ml. would be the alteration in volume produced by absorption of the carbon dioxide in 100 ml. of air. Even assuming that, by special precautions, the error of measurement were reduced to 1 in 10,000, there would still be an uncertainty of about 30 per cent. in the amount of carbon dioxide.

In practice, therefore, traces of gases are determined in a different manner. A large volume of the gas mixture is treated with a suitable absorbent, and the absorbed constituent is then determined by analysis of the reagent. For example, carbon dioxide in air may be determined by treating a large measured volume of air with a measured volume of standard baryta solution, and finding, by analysis, how much of the baryta has been converted into carbonate. The attainable accuracy is obviously greatly increased by the substitution of a chemical determination of the carbonate for the measurement of a minute alteration in a large volume. A comparatively rough measurement of the total volume is usually sufficiently accurate for a process of this kind.

Measurement of the Gas Mixture.—From the nature of the process no general rules can be laid down. For the measurement of any gas or other gas of which a large supply is available, the gasometer is most convenient. The special description of the determination of carbon dioxide in air (see p. 495) may be modified so as to be adapted to other cases.

Absorption Apparatus.—Convenient forms of apparatus for holding the absorption reagent are shown in Fig. 89, A,

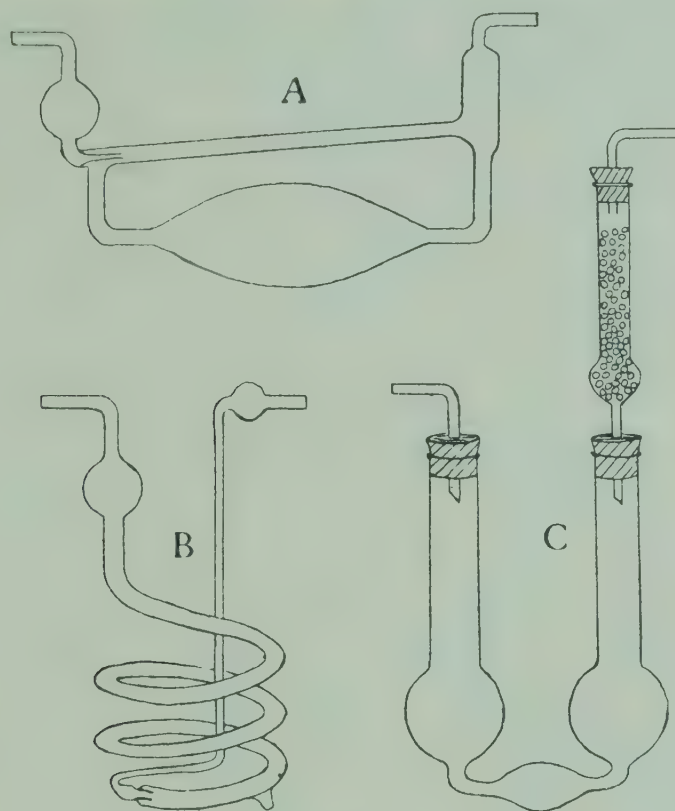


FIG 89

B, and C. If the gas contains dust, it must be passed through a tube packed with glass wool.

Sulphur in Coal Gas

OUTLINE OF METHOD.—The coal gas is burned in air and the sulphur dioxide formed is absorbed by a solution of sodium carbonate and bromine. All the sulphur is thereby obtained as sodium sulphate, and the sulphate is determined gravimetrically in the ordinary manner.

The gas is measured by a gas-meter and is led by the tube A into the glass flask B (Fig. 90). This is a 1-litre, round-bottomed, hard-glass flask with a short, wide mouth. The inlet tube must be of hard glass, and is drawn to a fine jet C where the gas is burned. The air required for the combustion of the gas is freed from any traces of hydrogen sulphide laboratory atmosphere by passing it through the filled with pumice, upon which a concentrated potassium hydroxide is constantly dropping from. The purified air then passes by the tube D. The products of the combustion are drawn off

means of a filter-pump through the tube F, and through three wash-bottles G, H, K, in which the sulphur dioxide is retained. The wash-bottles each contain sodium carbonate solution. To G and H a few drops of bromine are also added in order to oxidise the sulphite to sulphate.

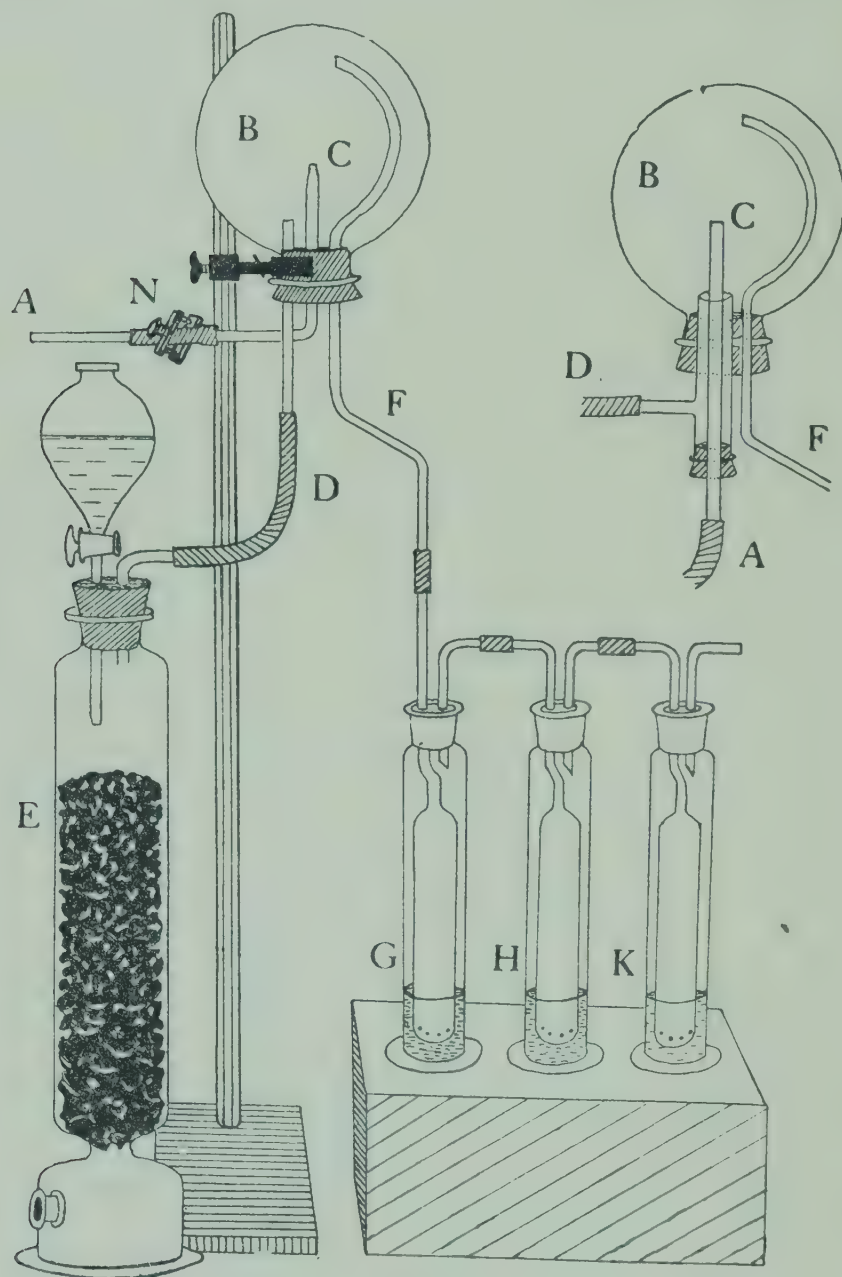


FIG. 90.

larger, steady flame may be obtained by the modified
 ent of the gas and air supplies shown at the side of
 The gas is led in through the central tube and
 the outer tube.

pur-ss coal gas through the meter for a few
 is gas at a Bunsen temporarily connected

to C. Disconnect the Bunsen, and ignite the gas at C. By means of the screw-clip N, cut down the gas supply until the flame is about 10 mm. high; then insert the stopper in the flask. By regulation of the air and gas supplies, adjust the flame so that it burns with sharply defined edges.

When about 50 litres of gas have been burned, cut off the gas supply. Wash the contents of the wash-bottles G and H into a beaker, and rinse the flask B into the same beaker. Acidify the solution with hydrochloric acid, boil until the excess of bromine is expelled, and determine the sulphate gravimetrically as barium sulphate.

It is advisable to test the bromine used, because it sometimes contains sulphuric acid.

Atmospheric Carbon Dioxide

OUTLINE OF METHOD.—The sample of air, contained in a dry bottle of known capacity, is shaken with a measured volume of standard baryta solution which contains also barium chloride, until the absorption of the carbon dioxide is complete. The excess of barium hydroxide is determined by titration with standard hydrochloric acid, these operations being conducted in such a way that the baryta is protected from expired air. The process depends upon the insolubility of barium carbonate during the titration of the excess baryta with very dilute acid.

The following solutions are required :—

Fiftieth-normal Hydrochloric Acid.—Acid of approximately this concentration can be obtained by diluting 9.5 ml. of the concentrated acid to 250 ml., and again diluting 25 ml. of the latter to 500 ml. It is then standardised by means of borax, using methyl red as indicator, or by titration with standard baryta.

Fiftieth-normal Baryta.—Prepare this as described on p. 95, but only about 60 ml. of saturated baryta will be required for 1 litre of N/50 solution, and the barium chloride content should be about 40 grams per litre in order to reduce the solubility of barium carbonate.

The absorption bottle is a Winchester quart, the capacity of which has been previously determined. It is fitted with a rubber stopper with two holes, into one of which a delivery tube is fitted, and a piece of glass rod is selected which fits fairly tightly into the other.

Collecting the Sample.—By means of a bellows pump, fill the bottle with the air to be analysed.

taken that expired air is not drawn into the bottle. Close the bottle with the rubber stopper, turning off the tap and closing the second hole with the glass rod. Note the temperature at the time of collection. (The error that may be introduced by assuming that the pressure is 760 mm. is less than other errors inherent in the method.)

Procedure.—Open the tap *out of doors* and immediately return the bottle to the laboratory, remove the glass rod and add about 2 ml. of phenolphthalein solution. Then at once run in 25 ml. of the baryta solution from the baryta burette through the hole from which the glass rod was removed. If a baryta burette outfit is not available the solution can be added from a pipette, but this must be operated by suction from the water pump or means adopted to avoid contact with expired air. A volume of 25 ml. of 0.02N baryta will be sufficient to absorb nearly five times the carbon dioxide content of outside air if the sample is taken in a Winchester quart, but more baryta should be used if the sample contains much more carbon dioxide than normal outside air. This would be indicated by the colour of the phenolphthalein disappearing altogether or becoming noticeably less. As soon as the baryta has been added, close the tap and replace the glass rod. Wet the whole of the inside of the bottle with the baryta solution, lay the bottle on its side, and shake it at frequent intervals during at least one hour. Then determine the excess of baryta by opening the tap, removing the glass rod and inserting the tip of the hydrochloric acid burette through the rubber stopper and titrating. The acid should be run in slowly, taking care to mix the contents of the bottle continuously to avoid a local excess of acid which might dissolve a little barium carbonate. Run the acid in until the pink colour of the phenolphthalein is almost discharged. Then remove the burette and allow the contents of the bottle to flow all over the inside, placing the glass rod in the open hole in the stopper to prevent entrance of carbon dioxide. It will be found that the baryta adhering to the sides of the bottle will cause the return of the pink colour. Run acid from the burette very slowly until this colour is just discharged. After the sides of the bottle have again been wetted. The burette has been read a measured volume of baryta solution is titrated by the acid at once, in an aliquot portion of the sample is carbon dioxide. This can be done by

adding, say, 10 ml. of the baryta solution to the bottle, *without* pouring out the liquid from the previous titration, and titrating with the acid. In this way any small error due to the action of a local excess of hydrochloric acid on barium carbonate near the end-point will be compensated for by a similar effect in titrating the additional barium hydroxide.

Example—

The volume of baryta solution added was 25 ml.

The volume of 0.0205N hydrochloric acid required for the excess of baryta was 19.54 ml., and the volume of acid required for an additional 25 ml. of baryta was 23.25 ml.

Hence (23.25—19.54) ml. of 0.0205N hydrochloric acid is equivalent to the carbon dioxide contained in the sample of air.

Now 1 ml. of N HCl is equivalent to 11.13 ml. of CO₂ at N.T.P.

Therefore 3.71 ml. of 0.0205N HCl is equivalent to $11.13 \times 3.71 \times 0.0205 = 0.847$ ml. of CO₂.

The volume of the Winchester quart was 2575 ml., so that the sample of air taken was (2575—25) ml. = 2550 ml., and the temperature was 15° C. The carbon dioxide in the sample of air was therefore—

$$\frac{0.847 \times 10,550}{2550} = 3.44 \text{ vols. in 10,000 vols. of air.}$$

(10,550 volumes at 15° are equal to 10,000 volumes at 0° C.)

If the sample was collected at a temperature greatly exceeding the temperature of the laboratory, a correction may be made for the amount of carbon dioxide that enters the bottle with the outdoor atmospheric air (containing about 3 parts of carbon dioxide in 10,000) when the bottle is opened at the start of the analysis. For a temperature difference of 10°, correction is approximately equivalent to a deduction of volume of carbon dioxide in 10,000 volumes of air.

Note.—The sample of air should not be taken by water out of the bottle in the atmosphere to be carbon dioxide may be given up by the water, the temporary hardness is high. The error more than 100 per cent.

Hydrogen Sulphide in Coal Gas

After measurement of its volume, the gas is dried by passing it over calcium chloride. The hydrogen sulphide is then absorbed by passing the gas through U-tubes containing pumice impregnated with copper sulphate and, at the exit end, a little calcium chloride. The pumice is prepared for use by soaking it in a hot, saturated copper sulphate solution and then drying it for four hours at 150° to 160°.

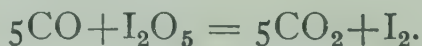
The increase in weight of the U-tubes gives the amount of hydrogen sulphide.

Sulphur Dioxide in Flue Gases

A measured volume of the gas is drawn through a tube containing cotton-wool to remove dust and then through a solution of sodium carbonate and bromine (see p. 494). The sulphate formed is determined gravimetrically.

Determination of Carbon Monoxide (in Traces)

For this purpose the gas is passed over heated iodine pentoxide, which reacts with the carbon monoxide according to the following equation :—



A measure of the amount of carbon monoxide present is obtained by titration with very dilute thiosulphate of the iodine formed. Unsaturated hydrocarbons, and reducing gases, such as hydrogen sulphide or sulphur dioxide, must first be removed from the gas. Contact with organic matter must be avoided, so the tube containing the iodine pentoxide must be carefully cleaned, and no greased stoppers or corks used.

Procedure.—Fill a U-tube, without taps but with side tubes, with alternate layers of iodine pentoxide and broken glass, and seal the wide ends. Place this in a bath of oil which is maintained at 150°. Connect one side tube to an aspirator tube such as that illustrated in Fig. 89 A, p. 493. The aspirator is filled with 10 per cent. potassium iodide solution to absorb the iodine. The gas entering the left limb drives the liquid of methane into the right limb, and thus causes it to circulate while the carbon dioxide is absorbed. The tubes must be touching in

order to minimise the amount of rubber surface exposed. A train of wash-bottles is fitted up, the first containing fuming sulphuric acid, the second ordinary concentrated sulphuric acid, and the third concentrated potassium hydroxide solution. This last is connected to the entrance tube of the iodine pentoxide vessel. The purpose of these reagents is to absorb any unsaturated hydrocarbons, sulphur dioxide or hydrogen sulphide. Select an aspirator bottle (K, p. 329) equal in volume to that of the gas to be passed, and fill it with water. Connect this with the exit tube of the potassium iodide absorption tube, attaching a screw-clip to the rubber connection.

Draw a slow current of the gas through the whole apparatus until the aspirator bottle is empty, this being made possible by a long exit tube attached to the aspirator bottle, to give the necessary fall of water.

Disconnect the potassium iodide tube, wash out the contents into a beaker and titrate the iodine by means of N/1000 sodium thiosulphate. Calculate the percentage of carbon monoxide, assuming the volume of gas passed is that of the aspirator bottle.

PART VIII

PHYSICO-CHEMICAL METHODS

DURING the last twenty or thirty years many physico-chemical methods of separation and analysis have been proposed in which the common feature is the utilisation of some physical property such as solubility, ionisation potential, mass, conductivity, radioactivity, and so on. Some of the methods are very sensitive and are most useful for the determination of traces of substances. Others permit the determination of certain substances without initial chemical separation, and are hence not liable to error from loss of material in a separatory process. The accuracy attainable varies from method to method, but is not always as good as that attainable by gravimetric or volumetric methods; in the determination of trace quantities, however, this is not of great importance. Some methods have the advantage that the results may be mechanically recorded and preserved for reference. In the following pages a brief outline of some of the more important of these techniques is given.

Applications of Radioactivity

The measurement of the disintegration rate in the process of radioactive decay has provided a very sensitive method for the determination of elements which possess radioactive isotopes of suitable half-life. The development of methods for the preparation of artificial radioactive isotopes has greatly increased the scope and usefulness of this method of analysis. Methods involving radioactivity permit the detection of amounts of material as small as 10^{-12} g. They may be grouped under three headings.

Tracer Techniques.—The investigation of the behaviour of a particular element in a chemical separation or analysis can be greatly simplified by adding to the system a radioactive isotope of the element and measuring the radioactivity of all the fractions obtained in the process. Typical applications of the method are the investigation of c^{us} and post-precipitation, tube.

the aging of precipitates, the separation of elements by partition and ion-exchange chromatography, and the measurement of partition coefficients.

Isotopic Dilution.—This method is often applicable to the analysis of systems for which no satisfactory chemical separation procedures are available. If the weight, x , of an inactive substance present in a mixture is to be determined, a known weight, y , of this substance, containing a known amount of a radioactive isotope, is added to the mixture. A chemically pure sample of the substance is isolated, without regard to the percentage recovery. The specific activity, in units of radioactivity per unit weight, of the added material and of the pure sample isolated is determined. Let it be S_a for the added material and S_i for the pure substance isolated. The specific activity of the isolated fraction is obviously $y/(x+y)$ times that of the added material.

$$S_i = \frac{y}{(x+y)} S_a.$$
$$x = y \left(\frac{S_a}{S_i} - 1 \right).$$

The method of isotopic dilution is particularly useful in organic analysis and in the investigation of complex biochemical systems.

Activation Analysis.—In this method, the weighed sample and a standard of similar composition containing a known weight of the element to be determined are irradiated together in a chain-reacting pile. It is assumed that both are exposed to the same flux of neutrons. After irradiation the sample and standard may be left for a time to allow shortlived and unwanted activity to decay. The sample and standard are then dissolved and a known weight of the element to be determined is added to both as a carrier. It is then ensured that exchange occurs between the radioactive isotope and the carrier or that both the active element and the carrier are present in the same oxidation state. The element to be determined is then isolated by standard chemical methods; when isolated it should be radiochemically pure. The chemical yield and the specific activity of sample and standard are then determined, and finally the radiochemical purity of the isolated compound is checked by examination of

its decay curve. The amount of the element in the sample is then calculated by simple proportion from the amount in the standard and the specific activities of the compounds isolated from the sample and standard.

Polarography

If a solution containing a mixture of metal salts is electrolysed in a cell which has a pool of mercury as the anode and mercury dropping slowly from a capillary as the cathode, and the applied potential is gradually increased, the current does not increase proportionately, but rises in a series of steps which are produced by substances reducible at the cathode. The shape of the curve is independent of the rate of change of voltage. The voltage at which a step occurs is characteristic for a particular ion, and the height of the step, *i.e.* the increase in current, is proportional to the concentration of that ion in the solution. Similar steps can be obtained by oxidation of some substances at a dropping mercury anode. In practice, the useful voltage range for oxidation or reduction is restricted, and ranges from about -2.5 to $+0.3$ volts.

The theory of polarography is rather complicated. A full account will be found in Kolthoff and Lingane's *Polarography*. Briefly, the method depends on concentration polarisation of the dropping mercury electrode and measurement of the diffusion current. A metal ion in solution will not be deposited on the cathode as metal and no current will flow until the potential between the solution and the cathode reaches a certain critical value. As the potential increases above this value the rate of reduction and the flow of current increase until a thin layer of solution round the cathode has been depleted of the ion being reduced. The current is then limited by the rate of diffusion of reducible ions through this layer. The rate of diffusion depends on the concentration and diffusion constant of the ion in the solution, the potential difference between the boundaries of the diffusion layer, and the viscosity of the solution. If the solution contains a large concentration of other ions (usually supplied by addition of what is known as a supporting electrolyte), the potential difference across the diffusion layer is negligible and the rate of diffusion remains constant as the potential is increased. The limiting current, known as

the diffusion current, is also independent of increases in potential. The viscosity can be kept constant by keeping the temperature and the composition of the solution constant. The diffusion current is then proportional to the concentration of the ion in the solution, and hence the amount of an ion present in a solution can be determined by comparing the diffusion currents in the solution and in a standard solution of known concentration. The diffusion current is simply measured from the height of the step in the current/applied voltage curve. The voltage at which half the diffusion current is reached is characteristic of the particular ion concerned, and is referred to as the half-wave potential. If their half-wave potentials are not too close a series of metals may be determined in the same solution.

Amperometric Titration.—The polarograph may be applied to the detection of the end-point of volumetric procedures involving precipitation, complex-formation, neutralisation, and oxidation-reduction. As the titration proceeds the electro-reducible substance is removed from the solution, and the diffusion current steadily decreases until it reaches a constant value provided the titrant is not electro-reducible or electro-oxidisable. If the diffusion current is plotted against volume of titrant added, two straight lines are obtained; the point of intersection of these lines represents the end-point of the titration. Since it is the current that is measured in this procedure, it is customary to refer to the method as amperometric titration.

For exercises suitable for practice see for example Milner, *Metallurgia*, 1947, **36**, 287 (polarography of lead in brass) and Laitinen, *Anal. Chem.*, 1949, **21**, 66 (review of amperometric titrations).

Chromatography

When a solution containing several adsorbable substances is passed through a column of a given adsorbent, the solutes will generally be held on the column. If now the column is treated with a suitable eluant, that is, a solvent which desorbs the substances from the column, a sequence of desorptions and adsorptions will take place, analogous to that which occurs in a fractionating column. The less strongly adsorbed (and hence more easily eluted) substances will move down the column more rapidly than those strongly adsorbed. If suitable eluants

are chosen it is possible to elute the adsorbed substances from the column one by one. The process of separation by treatment with an eluant is referred to as "development" of the chromatogram.

It is generally found that development separates the substances in bands which travel down the column. If the bands are coloured their position is obvious. If they are colourless their position may be detected by various methods such as irradiating the column with ultra-violet light and observing any fluorescence, or by treating the column with a reagent which will form coloured compounds with the separated substances.

In the technique known as partition chromatography, the solute is repeatedly partitioned between two solvents, one of which is kept stationary on a column of solid adsorbent (such as silica gel, paper, or rubber) while the other flows past it. This is really a special case of solvent extraction.

For an exercise in chromatography see for example, Ryan and Williams, *Analyst*, 1952, 77, 293.

In ion exchange, the adsorbent is usually a synthetic resin which has a number of polar groups at the surface. Resins intended for use as cation exchangers have acidic groups such as $-\text{COOH}$ or $-\text{SO}_3\text{H}$, whereas anion exchangers have basic groups such as the quaternary ammonium or $-\text{NH}_2$ group. For many analytical purposes, a strong acid cation exchanger with $-\text{SO}_3\text{H}$ groups and a strong base anion exchanger with $-\text{NOH}$ groups suffice. Both can be used in acid and alkaline solutions. When a solution containing a number of cations is passed through a column of a cation exchanger, the cations in the solution are exchanged at the resin surface for the cations originally on the surface. If a neutral solution of metal chlorides under appropriate conditions is passed through a column of cation exchanger in the hydrogen form (*i.e.* the exchangeable ions in the resin are hydrogen ions) the metal ions will be replaced in the solution by hydrogen ions and an equivalent amount of hydrochloric acid will be formed. The hydrochloric acid can be titrated and the amount of chloride present in the solution calculated.

In the case of an anion exchanger the anions originally present in the solution can be replaced by a single anion. Determination of this anion permits the determination of the sum of the equivalents of the anions originally present.

Ion exchangers are particularly useful in analytical chemistry for the removal of interfering substances from solution. Examples are the replacement of interfering metal ions (*e.g.* ferric iron) by hydrogen ions in the determination of sulphate by precipitation as barium sulphate, and the removal of phosphate ions before the determination of calcium by titration with EDTA.

Determination of Sulphur in Pyrites

The method given on p. 429 is modified by removing the interfering cations by ion exchange instead of precipitation.

Procedure.—Weigh out accurately by difference into a small porcelain basin not more than 100 mg. of pyrites, and add 2 ml. of bromine-carbon tetrachloride mixture (1 : 3). Cover the basin and set it aside in a fume-cupboard for 15 minutes, then add 2 ml. of concentrated nitric acid and again leave it for 15 minutes. Stir the contents of the basin at intervals during the next half-hour. Heat the basin cautiously on a steam-bath to expel bromine and carbon tetrachloride, and then evaporate off the nitric acid, also on the steam-bath. To the dry residue add 2 ml. of concentrated hydrochloric acid and evaporate to dryness again on the steam-bath to eliminate nitrate. Dissolve the residue in 1 ml. of concentrated hydrochloric acid and 9 ml. of water, heat, and filter through a 7 cm. Whatman No. 40 paper into a small beaker. Wash the basin and filter with about 20 ml. of water.

Transfer the contents of the beaker to a column of cation exchange resin that has been back-washed and converted into the hydrogen form as described below. Rinse the beaker with a little water and transfer the rinsings to the column. Allow the solution to flow down the column at the rate of 20 ml. per minute, and collect the effluent in a beaker. Without stopping the flow, wash the column 6 times with 20 ml. portions of distilled water, allowing each wash to drain until 1 cm. of liquid remains above the resin before adding the next portion of water. The resin should never be exposed to the air.

Heat the effluent solution almost to boiling, add 100 mg. of picric acid dissolved in a little water, and then, quite quickly, add dropwise with stirring a hot solution containing an amount of barium chloride that is four times the weight of pyrites taken. Let the solution boil gently for 10 minutes, then cool it under

the tap. Filter through a weighed small Gooch crucible or a weighed sintered porcelain crucible, dried at 160° . Wash the beaker and precipitate with cold water. Dry the crucible and precipitate at 160° for one hour, cool, and weigh. Repeat the drying and weighing until constant weight is attained. Calculate the percentage of sulphur in the pyrites.

Preparation of Resin Column.—Cover 25-30 g. of cation exchange resin (*e. g.* Zeokarb 215) with water in a beaker and leave it until it has swollen completely. Transfer the suspension to a column (the type of column used for a Jones reductor, p. 138, is suitable) at the bottom of which is a pad of glass wool. The resin must be kept covered with water.

Back-washing of Column.—This procedure is applied when the resin becomes too tightly packed or when air has been allowed to enter the column. Fit up the apparatus as shown at B in Fig. 91, and allow water to pass up through the column at a slow rate so as to agitate the resin without expelling it. Stop the flow, disconnect from the water tap and allow water to flow out until 1 cm. depth of it remains above the resin surface.

Regeneration of Resin.—After the resin has been used for the adsorption of cations from a solution it must be reconverted into the hydrogen form. Pass 350 ml. of 2N hydrochloric acid through the column at the rate of 20 ml. per minute, and then 200 ml. of distilled water. The column is then ready for use. The arrangement shown at A in Fig. 91 may be used for the regeneration process.

Solvent Extraction

A method that is often used for the isolation of one component of a mixture or for the removal of interfering substances is extraction from solution by a solvent that is immiscible with the solution. Some examples of this method have already been given in the section on colorimetry (pp. 292, 298, 303). Usually the substance extracted is an organometallic compound of the chelate type such as aluminium oxinate or acetylacetonate; sometimes, however, an inorganic compound can be successfully extracted as, for example, the ferric chloride from hydrochloric acid solution by means of ethers.

The extraction must be specific; that is, if the substance

to be determined is extracted only a negligible amount of other substances (or at any rate of substances that will interfere in the

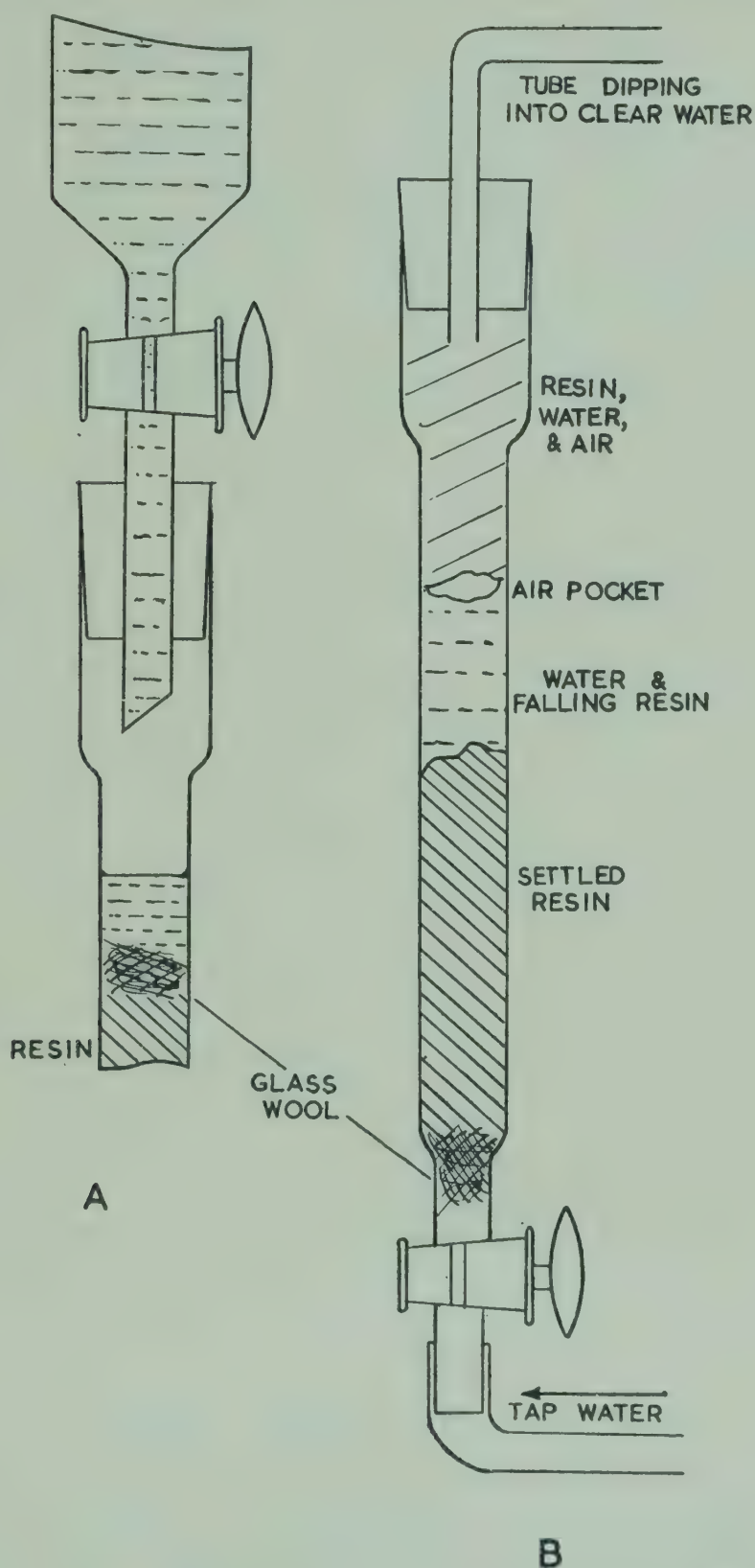


FIG. 91.

final process of the determination) must be extracted, and if interfering substances are being removed by extraction, only a negligible amount of the substance to be determined must be

extracted. It is desirable that the partition coefficient should be high enough for the extraction to be essentially complete in three extractions at most, and preferably in one. It has been found that in some cases (notably that of the ether extraction of ferric chloride) the efficiency of extraction decreases when only small amounts of the extractable substance are present.

The technique is particularly useful in analysis because of its rapidity. It is comparatively easy to obtain quantitative separation of the immiscible layers if the apparatus is properly designed. For cases in which the partition coefficient is not particularly favourable a number of automatic extractors have been designed and described in the literature.

Electrolysis with a Mercury Cathode

If a solution of metal salts is electrolysed in a cell in which the cathode consists of a pool of mercury, those metals which are produced at the cathode by reduction of their ions will amalgamate with the mercury. Since metal amalgams are generally less reactive than the metals themselves there is little reaction between the amalgam and the electrolyte, and the deposited metals are therefore effectively removed from the solution. This may be regarded as a special case of solvent extraction. The method is useful for the removal of large amounts of interfering elements and may be used under certain conditions to separate iron, nickel, cobalt, chromium, zinc, cadmium, copper, silver, gold, tin, molybdenum, thallium, germanium, bismuth, gallium, and some of the platinum metals, which are deposited, from aluminium, titanium, zirconium, vanadium, and uranium, which are not. It is usual to electrolyse a solution of the sulphates containing 0.15 to 0.30 ml. of concentrated sulphuric acid in 50 to 100 ml. of solution.

Electrolysis at Controlled Potential

For each element that can be electrodeposited from aqueous solution there is a decomposition voltage below which no deposition can occur. If the electrode potential can be controlled so that a constant voltage is applied to the electrolytic cell, it is possible to separate certain elements from admixtures with others. The method may be applied in analysis to the determination of elements or the separation of interfering

substances. In recent years a number of potentiostats have been described in the literature. (See, for example, Milner and Whittem, *Analyst*, 1952, 77, 11.)

Automatic Gravimetric Analysis

With the advent of thermobalances (that is, balances which automatically record the change in weight of a substance as it is heated, and plot the weight of the substance against the temperature) the possibility of developing automatic gravimetric procedures has become a reality.

The thermobalance permits the investigation of the behaviour of substances when they are heated; by its use decomposition temperatures can be accurately determined, and the temperature ranges within which substances remain stable may be found. The results obtained convey no information, however, as to the stability or hygroscopicity of a thermally stable substance when it has been cooled. For automatic analysis, where the substance is weighed while it is still at the temperature of ignition, this last point is without significance.

In principle, the method consists of weighing and decomposing the sample, and precipitating the desired constituent quantitatively and immediately in a form that does not require to be aged, can be rapidly filtered off, dried quickly, and converted into a stable weighing form at a relatively low temperature. The determination of the weight of the precipitate is very simple. The empty filter crucible is weighed at the temperature selected for the ignition, the weight being represented by a horizontal line on the record chart. A 50 mg. standard weight is added to the side of the balance carrying the crucible, and a second horizontal is recorded. The distance between the two lines represents, then, 50 mg. The crucible is removed from the balance, the precipitate is filtered off and washed, and the crucible is returned to the balance and ignited. The final horizontal line recorded when the crucible and precipitate have reached constant weight represents the weight of the crucible plus precipitate. The distance between this line and the line representing the weight of the crucible corresponds to the weight of the precipitate and can be evaluated by comparison with the distance obtained for the 50 mg. standard weight.

It is possible by these methods to complete a determination in as little as 20 minutes.

Emission Spectroscopy

The use of spectroscopy for the detection of elements has a long history. Quantitative analysis by means of the emission spectrum is a valuable tool in analytical chemistry; it is very sensitive, only small samples are required, it is applicable to most of the elements, and it is rapid in operation.

The intensities of the lines in the spectrum of an element differ, and generally the intensity of a given line is proportional to the concentration of the element in the sample being examined. As the sample is diluted the weaker lines disappear until a concentration is reached at which only the most intense lines persist. The concentration of an element can be determined by photographing the spectra for various dilutions of the sample, observing the lines that are left and comparing with dilutions of a standard sample. Alternatively, the spectrum may be photographed and the intensities of the lines compared photometrically with those of neighbouring lines of another element present in known constant amount.

The main difficulties in spectrochemical analysis are interference caused by other elements, and the problem of obtaining reproducible excitation conditions. Under the most favourable conditions agreement of results to within 1 per cent. is attainable, but more generally the error is of the order of 5 per cent.

Flame Photometry

The flame test for the alkali metals is well-known in qualitative analysis, and is a special case of emission spectroscopy. The gas flame is sufficiently hot to excite the spectra of the alkali metals, the alkaline earths, thallium, and molybdenum, but not those of other metals. The intensity of the lines of a spectrum increases with the temperature of the source of excitation. The temperature of a flame can be kept relatively constant, and a flame source of excitation can be used in the spectrochemical determination of those elements for which adequate sensitivity is attainable. If a normal air-gas flame is used, the alkali metals and calcium can be readily determined

by flame photometry. With an oxy-hydrogen or oxy-acetylene flame some 35 elements can be determined.

In practice the element to be determined is obtained in solution, and the solution is introduced into a flame in the form of a fine spray or mist by means of an atomiser operated at constant air pressure. The intensity of the coloration of the flame is then measured photometrically, a spectrophotometer or a filter photometer being used as the measuring instrument.

Two methods are available for the final measurement of the concentration of the element in the solution. In one the instrument used is calibrated by spraying a series of standard solutions of the element concerned, and measuring the flame intensities produced; the standards should have approximately the same composition as the samples used so that interference effects of other ions will largely cancel. The other method, known as the internal standard method, involves the addition of a known amount of another alkali metal, usually lithium, to the solution, and measurement of the intensity of the sodium or potassium spectrum in terms of the intensity of the lithium spectrum. Calibration is performed by means of a series of standard solutions as in the direct comparison method, except that lithium is added and the internal standard technique is applied. The internal standard method has the advantage that it automatically compensates for small fluctuations in the flame while measurements are being made and permits the attainment of a slightly better degree of precision. In general the error is of the order of 1 to 2 per cent.

For suitable exercises see, for example, Knight, Mathis, and Graham, *Anal. Chem.*, 1951, **23**, 1704; Biffen, *Anal. Chem.*, 1950, **22**, 1014.

High Frequency Titration

In recent years a new method for the detection of end-points in volumetric analysis has been developed. In general, the solution being titrated is placed in a glass vessel in such a position that it exerts a loading effect on some component of a high frequency oscillating circuit, and the change in some electrical property of the circuit is measured as the composition of the solution is altered by titration. Usually the electrical property measured is the frequency of the oscillations or the

grid current. The changes in these can be converted into terms of the changes in the effective conductance or the effective capacitance of the titration cell during the titration.

In some cases end-points can be detected more easily and more rapidly by this method than by others.

(For instruments see Blaedel and Malmstadt, *Anal. Chem.*, 1950, **22**, 734; for an exercise see Anderson and Revinson, *Anal. Chem.*, 1950, **22**, 1272.)

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- 2 *

APPENDIX

LIST OF COMMON REAGENTS

Unless the contrary is stated, it is to be understood that any reagent mentioned in the text has the composition and concentration indicated below. For convenience, the quantity necessary for the preparation of a Winchester of solution is given in each case. A Winchester contains about 2500 ml.

For quantitative work it is usually necessary to prepare solutions as required, since the bench solutions, even when prepared from the purest chemicals, usually contain appreciable amounts of impurities dissolved from the glass.

Acids and Alkalis

The dilute acids and alkalis are 2N, with the exception of barium hydroxide and calcium hydroxide.

Concentrated Sulphuric Acid (Specific Gravity 1.84) is approximately 36N. It often contains traces of lead, iron, and nitric acid.

4N Sulphuric Acid is prepared by diluting 270 ml. of the concentrated acid to a Winchester.

Dilute Sulphuric Acid (approximately 2N) is prepared by diluting 135 ml. of the concentrated acid to a Winchester.

Concentrated Nitric Acid (Specific Gravity 1.42).—This is the constant boiling-point acid and contains about 68 per cent. of nitric acid. It is about 16N. The commonest impurities are chloride and sulphate.

Dilute Nitric Acid (approximately 2N) is prepared by diluting 300 ml. of the concentrated acid to a Winchester.

Concentrated Hydrochloric Acid (Specific Gravity 1.17) is about 10.8N. It may contain traces of iron, arsenic, and sulphate.

Dilute Hydrochloric Acid (approximately 2N) is prepared by diluting 500 ml. of the concentrated acid to a Winchester.

Acetic Acid (approximately 2N) is prepared by diluting 280 ml. of glacial acetic acid (about 17N) to a Winchester.

Sodium Hydroxide (approximately 2N) is prepared by dissolving 200 grams of sodium hydroxide ("white sticks") in a Winchester. It always contains carbonate and chloride, and may also contain sulphate, alumina, and silica. If required pure, it must be prepared from metallic sodium or by electrolysis (p. 90) and stored in a plastic vessel.

Concentrated Ammonia (Specific Gravity 0.880) is about 18N. The commonest impurities are carbonate, silicate, and aluminate (derived from glass bottles), and tarry matter.

Dilute Ammonia (approximately 2N) is prepared by diluting 250 ml. of concentrated ammonia to a Winchester. If required specially pure, it can be prepared by dissolving the gas from a cylinder in well-cooled water, contained in a plastic container surrounded by a mixture of ice and water.

Ammonium Carbonate (approximately 2N) is prepared by dissolving 200 grams of commercial ammonium carbonate (sesqui-carbonate), together with 100 ml. of 0.880 ammonia, in a Winchester.

Sodium Carbonate (approximately 2N) is prepared by dissolving 250 grams of the anhydrous salt, or 680 grams of the decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$) in a Winchester. It usually contains traces of chloride and sulphate, and some samples are worthless on account of the amount of these impurities. It occasionally contains traces of ammonia.

Calcium Hydroxide (approximately 0.04N) is a saturated solution prepared from pure lime.

Barium Hydroxide (approximately 0.4N) is a saturated solution of barium hydroxide in water.

Other Common Reagents

Alcohol.—Rectified spirit contains 93 to 95 per cent. of ethyl alcohol. The "66 over-proof" spirit contains 93 per cent. of alcohol.

Ammonium Chloride (approximately 2N) contains 260 grams of the salt, NH_4Cl , in a Winchester.

Ammonium Molybdate (approximately 3 per cent.) contains 75 grams of the salt, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in a Winchester.

Ammonium Oxalate (approximately 0.5N) contains 85 grams of the salt, $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$, in a Winchester.

Ammonium Phosphate (approximately 0.5N) contains 55 grams of the salt, $(\text{NH}_4)_2\text{HPO}_4$, in a Winchester.

Ammonium Sulphide (approximately 2N) is prepared by saturating 1200 ml. of 2N ammonia with hydrogen sulphide, and then adding an equal volume of 2N ammonia.

Barium Chloride (approximately 0.5N) contains 145 grams of the salt, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, in a Winchester.

Barium Nitrate (approximately 0.5N) contains 150 grams of the salt, $\text{Ba}(\text{NO}_3)_2$, in a Winchester.

Bromine Water (approximately 0.5N) is a saturated solution. It usually contains chlorine and iodine as impurities.

Calcium Chloride (approximately 0.5N) contains 140 grams of the salt, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$, in a Winchester.

Calcium Sulphate (approximately 0.03N) is a saturated solution.

Copper Nitrate (approximately 0.2N) contains 70 grams of the salt, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in a Winchester.

Ferrous Sulphate (approximately N) is prepared by dissolving 335 grams of the salt, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, together with 300 ml. of dilute sulphuric acid, in a Winchester.

Ferric Chloride (approximately 0.2N) is prepared by dissolving 45 grams of the salt, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, in 50 ml. of concentrated hydrochloric acid and diluting to a Winchester.

Fusion Mixture is prepared by grinding in a mortar a mixture of anhydrous sodium and potassium carbonates in the ratio of their molecular weights, *i.e.* 106 to 138.

Hydrochloroplatinic Acid.—This is usually obtained as the hydrate $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, which contains 37.66 per cent. of platinum. In order to prepare a solution containing 10 per cent. of platinum (10 grams of platinum per 100 ml. of solution), dissolve 26.5 grams of this hydrate in about 50 ml. of water, filter, and wash the vessel and the filter two or three times with water. Dilute the filtrate and washings to 100 ml. The specific gravity of a solution containing 10 per cent. of platinum is 1.155 at 25°.

The preparation of this "10 per cent." solution from commercial platinum is described in Treadwell's *Analytical Chemistry*, vol. i. The recovery of platinum from residues by reduction with formic acid is described by M. Swisher (*Ind. Eng. Chem., Anal. Ed.*, 1939, **11**, 162).

Lead Acetate (approximately 0.5N) is prepared by dissolving 220 grams of the salt, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$, together with 30 ml. of glacial acetic acid, in a Winchester.

Mercuric Chloride (approximately 0.2N) contains 65 grams of the salt, HgCl_2 , in a Winchester.

Mercurous Nitrate is prepared by dissolving 125 grams of the salt in 200 ml. of dilute nitric acid and 1250 ml. of water, and diluting to a Winchester.

Potassium Ferrocyanide (approximately 0.2N) contains 50 grams of the salt, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, in a Winchester.

Potassium Chromate (approximately 0.2N) contains 50 grams of the salt, K_2CrO_4 , in a Winchester.

Potassium Iodide (approximately 0.1N) contains 40 grams of the salt, KI , in a Winchester.

Sodium Acetate (approximately N) contains 325 grams of the salt $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, in a Winchester.

Stannous Chloride (approximately 0.2N) is made by dissolving 60 grams of the salt, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, in 250 ml. of concentrated hydrochloric acid and diluting to a Winchester. A piece of tin placed in each bottle preserves the salt in the stannous state.

Silver Nitrate (approximately 0.1N) contains 40 grams of the salt, AgNO_3 , in a Winchester.

PREPARATION OF PURE GASES

Carbon Dioxide.—This gas is prepared in a Kipp generator from marble and 4N hydrochloric acid. It must be washed and dried by passing it through a solution of sodium bicarbonate containing some solid, and then through concentrated sulphuric acid.

Hydrogen.—Hydrogen is prepared in a small Kipp generator from 6N sulphuric acid and arsenic-free zinc. A little copper sulphate solution should be poured over the zinc before this is placed in the Kipp. The gas must be purified and dried by passing it through a solution of mercuric chloride, then through an alkaline solution of potassium permanganate, and finally through concentrated sulphuric acid. Before the hydrogen is used, it must be proved free from any appreciable amount of air by collecting a sample in a test-tube over water, and noting whether it burns quietly when ignited. If the gas must be oxygen-free, it must be passed over heated platinised asbestos before finally being dried with sulphuric acid.

Very pure hydrogen can be obtained by the electrolysis of barium hydroxide solution, using a platinum cathode. Traces of oxygen may be removed as above.

Oxygen.—Oxygen is prepared by heating potassium permanganate in a hard glass test-tube or small flask.

Any of these gases may be obtained in an almost pure condition from cylinders obtainable commercially.

Indicator Solutions

(See also p. 80.)

Bromo-phenol Blue.—Dissolve 0.5 gram in 1 litre of 20 per cent. alcohol.

Bromo-thymol Blue.—Dissolve 0.1 gram in water, add 1.6 ml. of 0.1N sodium hydroxide and dilute to 1 litre with water.

Cresol Red.—Dissolve 0.5 gram in 1 litre of 20 per cent. alcohol.

Litmus.—Dissolve 1 gram of azolitmin in 1 litre of water.

Methyl Orange.—Dissolve 0.05 gram of the solid in 1 litre of water.

Methyl Red.—Dissolve 0.05 gram of the solid in 800 ml. of alcohol, and dilute to 1 litre with water.

Methyl Yellow.—Dissolve 0.1 gram in 800 ml. of alcohol, and dilute to 1 litre with water.

Phenolphthalein.—Dissolve 1 gram of the solid in 500 ml. of alcohol, and dilute to 1 litre with water.

SOLUTIONS FOR ANALYSIS

It is customary for beginners to perform their first quantitative exercises with pure salts of known composition. There are many objections to this system—the most serious is that the exercise does not imitate the conditions met with in ordinary practice. For example, when working with a known quantity of material, the problem of how much precipitant to add does not, as a rule, present any difficulty; in this important particular, therefore, the exercise lacks much of the educational value it should possess. For this reason alone, it is desirable that all quantitative exercises should be performed with solids or solutions of “unknown” composition.

The most convenient system whereby a number of students can be provided with different exercises is to use standard solutions, and the following list may be found serviceable. All the solutions mentioned below can be prepared by weight from substances that are obtainable commercially in a pure state. The quantities given are the amounts required for the preparation of 1 litre of solution. The solid should be dissolved in distilled water unless otherwise stated. With these concentrations, 20 to 30 ml. is a suitable quantity for an analysis.

Aluminium	. 70 grams of ammonium alum, $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{Al}_2\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.
Ammonia	. 40 grams of ammonium chloride, NH_4Cl .
Antimony	. 16 grams of tartar emetic, $\text{C}_4\text{H}_4\text{O}_6\text{KSbO} \cdot \frac{1}{2}\text{H}_2\text{O}$.
Arsenic	. 6 grams of arsenious oxide, As_2O_3 , dissolved in dilute hydrochloric acid.
Barium	. 20 grams of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.
Bismuth	. 10 grams of bismuth oxychloride, BiOCl , dissolved in 200 ml. of concentrated hydrochloric acid, and diluted to 1 litre.
Borate	. 20 grams of borax, $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$.
Bromide	. 15 grams of potassium bromide, KBr .
Cadmium	. 15 grams of cadmium sulphate, $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$.
Calcium	. 20 grams of pure calcspar, CaCO_3 , dissolved in dilute hydrochloric acid.
Carbonate	. 100 grams of uneffloresced crystals of sodium carbonate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.
Chlorate	. 2 grams of potassium chlorate, KClO_3 .
Chloride	. 20 grams of barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$.
Chromate	. 20 grams of potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$.
Chromium	. 50 grams of chrome alum, $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.
Cobalt	. 20 grams of cobalt nitrate, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.
Copper	. 30 grams of copper sulphate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.
Ferrocyanide	. 45 grams of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$.
Iodide	. 20 grams of potassium iodide, KI .
Iron	. 50 grams of ferric alum, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$.
Lead	. 20 grams of lead nitrate $\text{Pb}(\text{NO}_3)_2$. It is advisable to recrystallise this salt from a dilute nitric acid solution.
Lithium	. 11 grams of lithium carbonate, Li_2CO_3 , dissolved in dilute hydrochloric acid.
Magnesium	. 25 grams of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.

Manganese	. Dissolve 20 grams of pure potassium permanganate in water, and pass sulphur dioxide through the solution until it is completely decolorised and the precipitated manganese dioxide has dissolved. Boil until free from sulphur dioxide, and dilute to 1 litre.
Mercury	. 10 grams of red mercuric oxide, HgO , dissolved in concentrated nitric acid, boiled, and diluted to 1 litre.
Nickel	. 70 grams of nickel ammonium sulphate, $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$.
Nitrate	. 16 grams (for reduction method) or 2.5 grams (for oxidation method) of potassium nitrate, KNO_3 .
Phosphate	. 1.23 gram of microcosmic salt, $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ (for the molybdate method).
Potassium	. 15 grams of potassium chloride, KCl .
Silver	. 20 grams of silver nitrate, AgNO_3 .
Strontium	. 22 grams of strontium chloride, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$.
Sulphate	. 25 grams of magnesium sulphate, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.
Zinc	. 30 grams of zinc sulphate, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$.

TYPICAL ANALYSES

Various Glasses

	SiO ₂ .	PbO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	B ₂ O ₃ .	ZnO.	Total.
Plate glass .	71.72	...	1.29	0.13	15.54	11.49	100.17
Flint glass .	42.85	43.2	0.2	0.05	0.20	...	13.70	100.2
Glass for chemical ware	(1) 66.2	...	2.4	0.13	0.4	9.77	1.2	10.3	9.5	99.9
	(2) 80.2	...	2.5	0.11	0.2	4.10	0.57	12.5	...	100.18

Various Silicates

	SiO ₂ .	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
Albite .	68.80	...	19.43	...	0.20	nil	11.68	...	100.11
Albite .	67.99	...	19.23	...	1.84	1.25	9.69	...	100.00
Albite .	68.40	...	19.89	0.90	10.69	...	99.88
Orthoclase .	66.56	...	19.18	...	0.52	6.94	6.56	...	99.76
Orthoclase .	66.58	...	21.26	...	1.18	0.76	10.26	0.16	100.20
A clay .	63.69	...	17.02	10.18	0.97	...	4.02	4.05	99.93
Talc .	63.42	31.49	...	0.57	4.38	99.86
Talc .	62.78	31.16	...	1.85	4.32	100.11

Iron Pyrites

S.	Cu.	Fe.	Mn.	Zn.	Insoluble residue.	Total.
43.03	2.50	39.54	0.06	0.42	14.68	100.23
42.59	1.49	40.11	0.03	0.72	15.01	99.95
53.37	2.39	44.47	100.23
52.71	0.24	44.23	2.58	99.76
48.73	...	42.94	...	0.18	7.82	99.67

Dolomite

CaO.	MgO.	CO ₂ .	Fe ₂ O ₃ +Al ₂ O ₃ .	FeO.	H ₂ O.	Insoluble residue.	Total.
29.51	20.29	47.22	0.82	...	1.05	1.33	100.22
30.75	25.18	42.01	...	0.83	0.07	1.30	100.14
29.61	12.94	44.72	...	12.99	100.26

Portland Cement

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	SO ₃ .	CO ₂ +H ₂ O.	Alkalis.	Insoluble residue.	Total.
21·88	6·26	3·20	63·92	1·17	1·42	1·40	0·43	0·22	99·90
24·40	4·76	2·43	64·70	1·20	1·30	0·56	0·64	0·15	100·14
21·76	6·77	3·43	62·56	1·14	1·25	1·72	0·69	0·75	100·07

Cassiterite

SnO ₂ .	Fe ₂ O ₃ .	CaO.	SiO ₂ .	Total.
98·74	0·12	0·41	0·19	99·46

Cassiterite often contains traces of As and Zn.

Garnet

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	H ₂ O.	Total.
40·92	22·45	5·46	8·11	0·46	17·85	5·04	0·10	100·39

Traces of Cr are usually found in garnets.

Manganese Minerals

	MnO ₂ .	MnO.	Fe ₂ O ₃ .	BaO.	H ₂ O.	Insoluble residue.	Total.
Pyrolusite . .	86·45	6·02	0·93	1·31	1·22	4·11	100·04
Pyrolusite . .	69·06	18·16	0·55	...
Manganite . .	48·47	42·03	7·41	1·72	99·63

Zinc Blende

S.	Zn.	Cd.	Fe.	Mn.	Pb.	Total.
32·98	64·92	1·05	0·57	0·37	0·15	100·04
33·25	50·02	0·30	15·44	nil	1·01	100·02

Copper Pyrites

S.	Fe.	Cu.	Ag.	Pb.	Insoluble residue.	Total.
30.50	21.08	48.40	trace	99.98
33.18	32.65	32.79	nil	0.35	1.04	100.01
36.15	29.34	32.25	nil	0.30	2.09	100.13

Specific Gravity and Concentration of Hydrochloric Acid at 15°

(Normal HCl = 36.47 grams per litre)

Specific gravity 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Normality.	Specific gravity 15°/4°.	100 grams contain grams HCl.	1 litre contains grams HCl.	Normality.
1.010	2.14	22	0.6	1.110	21.9	243	6.7
1.020	4.13	42	1.2	1.120	23.8	267	7.3
1.030	6.15	64	1.8	1.130	25.7	291	8.0
1.040	8.16	85	2.3	1.140	27.7	315	8.6
1.050	10.17	107	2.9	1.150	29.6	340	9.3
1.060	12.19	129	3.5	1.160	31.5	366	10.0
1.070	14.17	152	4.2	1.170	33.5	392	10.8
1.080	16.15	174	4.8	1.180	35.4	418	11.7
1.090	18.1	197	5.4	1.190	37.2	443	12.1
1.100	20.0	220	6.0	1.200	39.1	469	12.9

Specific Gravity and Concentration of Sulphuric Acid at 15°

(Normal H₂SO₄ = 49.04 grams per litre)

Specific gravity 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Normality.	Specific gravity 15°/4°.	100 grams contain grams H ₂ SO ₄ .	1 litre contains grams H ₂ SO ₄ .	Normality.
1.006	1	10.1	0.20	1.449	55	797	16.25
1.013	2	20.3	0.41	1.502	60	901	18.38
1.020	3	30.4	0.62	1.558	65	1013	20.65
1.026	4	41.0	0.84	1.615	70	1130	23.05
1.033	5	51.6	1.05	1.674	75	1248	25.60
1.040	6	62.4	1.27	1.732	80	1386	28.26
1.047	7	73.3	1.49	1.784	85	1520	30.92
1.054	8	84.3	1.72	1.820	90	1640	33.40
1.061	9	95.5	1.95	1.825	91	1660	33.86
1.068	10	106.8	2.18	1.829	92	1680	34.32
1.104	15	160.6	3.38	1.833	93	1710	34.76
1.143	20	228	4.66	1.836	94	1730	35.20
1.182	25	296	6.02	1.839	95	1750	35.62
1.222	30	367	7.48	1.841	96	1770	36.03
1.264	35	444	9.02	1.841	97	1790	36.42
1.306	40	522	10.66	1.841	98	1800	36.79
1.351	45	608	12.40	1.839	99	1820	37.13
1.399	50	700	14.26	(1.836)	100	(1836)	(37.4)

Specific Gravity and Concentration of Nitric Acid at 15°

(Normal HNO_3 = 63.02 grams per litre)

Specific gravity 15°/4°.	100 grams contain grams HNO_3 .	1 litre contains grams HNO_3 .	Normality.	Specific gravity 15°/4°.	100 grams contain grams HNO_3 .	1 litre contains grams HNO_3 .	Normality.
1.010	1.90	19	0.30	1.280	44.41	568	9.01
1.020	3.70	38	0.60	1.300	47.49	617	9.8
1.040	7.26	75	1.19	1.320	50.71	669	10.6
1.060	10.68	113	1.79	1.340	54.07	725	11.5
1.080	13.95	151	2.35	1.360	57.57	783	12.4
1.100	17.11	188	2.99	1.380	61.27	846	13.4
1.120	20.23	227	3.60	1.400	65.30	914	14.5
1.140	23.31	266	4.22	1.420	69.80	991	15.7
1.160	26.36	306	4.84	1.440	74.68	1075	17.1
1.180	29.38	347	5.51	1.460	79.98	1168	18.5
1.200	32.36	388	6.16	1.480	86.05	1274	20.2
1.220	35.28	430	6.83	1.500	94.1	1410	22.4
1.240	38.29	475	7.54	1.510	98.1	1480	23.5
1.260	41.34	521	8.25	1.520	99.7	1515	24.0

Specific Gravity and Concentration of Perchloric Acid at 15°

(Normal HClO_4 = 100.47 grams per litre)

Specific gravity 15°/4°.	100 grams contain grams HClO_4 .	1 litre contains grams HClO_4 .	Specific gravity 15°/4°.	100 grams contain grams HClO_4 .	1 litre contains grams HClO_4 .
1.030	5.25	54	1.240	33.85	420
1.060	10.06	107	1.270	37.08	471
1.090	14.56	159	1.300	40.10	521
1.120	18.88	212	1.360	45.71	622
1.150	22.99	264	1.420	50.91	723
1.180	26.82	316	1.540	60.04	925
1.210	30.45	369	1.675	70.15	1175

Specific Gravity and Concentration of Acetic Acid at 15°

Specific gravity 15°/4°.	100 grams contain grams CH_3COOH .	1 litre contains grams CH_3COOH .	Specific gravity 15°/4°.	100 grams contain grams CH_3COOH .	1 litre contains grams CH_3COOH .
1.002	2	20.04	1.062	50	530.8
1.005	4	40.21	1.065	55	585.9
1.011	8	80.9	1.069	60	641.1
1.014	10	101.4	1.071	65	696.3
1.021	15	153.2	1.073	70	751.3
1.028	20	205.7	1.074	75	805.9
1.035	25	258.8	1.075	80	859.8
1.041	30	312.4	1.074	85	912.8
1.047	35	366.5	1.071	90	964.2
1.052	40	420.9	1.066	95	1012.7
1.057	45	475.7	1.055	100	1055.3

Specific Gravity and Concentration of Potassium Hydroxide at 15°. (Eq. wt. = 56.10)

Specific gravity 15°/4°.	100 grams contain grams KOH.	1 litre contains grams KOH.
1.033	5	52
1.082	10	108
1.134	15	178
1.176	20	235
1.230	25	307
1.287	30	386
1.346	35	471
1.411	40	564
1.473	45	663
1.538	50	769

Specific Gravity and Concentration of Sodium Hydroxide at 15°. (Eq. wt. = 40.01)

Specific gravity 15°/4°.	100 grams contain grams NaOH.	1 litre contains grams NaOH.
1.058	5	53
1.113	10	111
1.170	15	175
1.224	20	245
1.279	25	320
1.332	30	400
1.383	35	484
1.433	40	573
1.481	45	666
1.529	50	765

Specific Gravity and Concentration of Ammonia Solutions at 15°

(Normal NH_3 = 17.03 grams per litre)

Specific gravity 15°/4°.	100 grams contain grams NH_3 .	1 litre contains grams NH_3 .	Normality.	Specific gravity 15°/4°.	100 grams contain grams NH_3 .	1 litre contains grams NH_3 .	Normality.
0.990	2.31	22.9	1.3	0.930	18.64	173.4	10.2
0.980	4.80	47.0	2.8	0.920	21.75	210.1	11.8
0.970	7.31	70.9	4.2	0.910	24.99	227.4	13.4
0.960	9.91	95.1	5.6	0.900	28.33	255.0	15.0
0.950	12.74	121.0	7.1	0.890	31.75	282.6	16.6
0.940	15.63	146.9	8.6	0.880	35.70	314.2	18.5

Specific Gravity of Aqueous Alcohol at 15°

Specific gravity 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.	Specific gravity 15°/4°.	Grams of alcohol per 100 grams.	Grams of alcohol per litre.
0.983	10	98	0.872	70	610
0.971	20	194	0.860	75	645
0.957	30	287	0.848	80	678
0.939	40	376	0.835	85	710
0.918	50	459	0.822	90	740
0.895	60	537	0.808	95	768
0.884	65	574	0.793	100	793

Weight of 1 Litre of Various Dry Gases at 0° and 760 mm.

	Grams.		Grams.
Air	1·2928	Methane	0·7170
Carbon monoxide	1·2506	Nitric oxide	1·3402
Carbon dioxide	1·9635	Nitrogen	1·2505
Hydrogen	0·0900	Oxygen	1·4292

Vapour Pressure of Water

Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.	Tempera- ture.	Vapour Pressure.
Degrees.	mm.	Degrees.	mm.	Degrees.	mm.
4	6·1	14	11·9	24	22·2
5	6·5	15	12·7	25	23·5
6	7·0	16	13·6	26	25·0
7	7·5	17	14·4	27	26·5
8	8·0	18	15·4	28	28·1
9	8·6	19	16·4	29	29·8
10	9·2	20	17·4	30	31·5
11	9·8	21	18·5	31	33·4
12	10·5	22	19·7	32	35·4
13	11·2	23	20·9	33	37·4

Vapour Pressure of Potassium Hydroxide Solutions

Temperature.	Vapour pressure of 40 per cent. solution.	Vapour pressure of 50 per cent. solution.
Degrees.	mm.	mm.
10	6·5	5·6
12	7·5	6·5
14	8·4	7·3
16	9·6	8·3
18	10·9	9·5
20	12·4	10·8
22	13·9	12·1

The “40 per cent.” solution is one containing 40 grams of potassium hydroxide added to 100 grams of water, and the “50 per cent.” solution one containing 50 grams of potassium hydroxide added to 100 grams of water.

Sintered Crucibles

Material of which crucible is made.	Grade of porosity.	Average size of pores (microns).	Temperature to which crucible may be heated.
Glass . .	0	200-250	580° maximum in an electric furnace. Cool to 200° or less before removing from furnace.
	1	100-120	
	2	40-50	
	3	20-30	
	4	5-10	
	5	1-1.5	
Porcelain .	4	5-15 (maximum)	1000° if heated and cooled slowly.
Silica . .	1	90-150	1000°
	2	40-90	
	3	15-40	
	4	5-15	

Logarithms

	0	1	2	3	4	5	6	7	8	9									
100	0000	0004	0009	0013	0017	0022	0026	0030	0035	0039									
101	0043	0048	0052	0056	0060	0065	0069	0073	0077	0082									
102	0086	0090	0095	0099	0103	0107	0111	0116	0120	0124									
103	0128	0133	0137	0141	0145	0149	0154	0158	0162	0166									
104	0170	0175	0179	0183	0187	0191	0195	0199	0204	0208									
105	0212	0216	0220	0224	0228	0233	0237	0241	0245	0249									
106	0253	0257	0261	0265	0269	0273	0278	0282	0286	0290									
107	0294	0298	0302	0306	0310	0314	0318	0322	0326	0330									
108	0334	0338	0342	0346	0350	0354	0358	0362	0366	0370									
109	0374	0378	0382	0386	0390	0394	0398	0402	0406	0410									
110	0414	0418	0422	0426	0430	0434	0438	0441	0445	0449	1	2	3	4	5	6	7	8	9
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8

Logarithms

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

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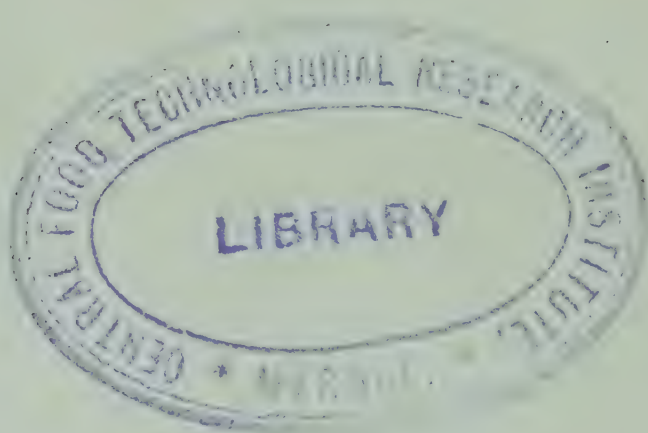
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International Atomic Weights, 1951¹

Aluminium . . . Al	26.98	Neodymium . . . Nd	144.27
Antimony . . . Sb	121.76	Neon . . . Ne	20.183
Argon . . . A	39.944	Nickel . . . Ni	58.69
Arsenic . . . As	74.91	Niobium (Colum- bium) . . . Nb	92.91
Barium . . . Ba	137.36	Nitrogen . . . N	14.008
Beryllium . . . Be	9.013	Osmium . . . Os	190.2
Bismuth . . . Bi	209.00	Oxygen . . . O	16.000
Boron . . . B	10.82	Palladium . . . Pd	106.7
Bromine . . . Br	79.916	Phosphorus . . . P	30.975
Cadmium . . . Cd	112.41	Platinum . . . Pt	195.23
Cæsium . . . Cs	132.91	Potassium . . . K	39.100
Calcium . . . Ca	40.08	Praseodymium . . . Pr	140.92
Carbon . . . C	12.011	Radium . . . Ra	226.05
Cerium . . . Ce	140.13	Radon . . . Rn	222
Chlorine . . . Cl	35.457	Rhenium . . . Re	186.31
Chromium . . . Cr	52.01	Rhodium . . . Rh	102.91
Cobalt . . . Co	58.94	Rubidium . . . Rb	85.48
Copper . . . Cu	63.54	Ruthenium . . . Ru	101.1
Dysprosium . . . Dy	162.46	Samarium . . . Sa	150.43
Erbium . . . Er	167.2	Scandium . . . Sc	44.96
Europium . . . Eu	152.0	Selenium . . . Se	78.96
Fluorine . . . F	19.00	Silicon . . . Si	28.09
Gadolinium . . . Gd	156.9	Silver . . . Ag	107.880
Gallium . . . Ga	69.72	Sodium . . . Na	22.991
Germanium . . . Ge	72.60	Strontium . . . Sr	87.63
Gold . . . Au	197.0	Sulphur . . . S	32.066
Hafnium . . . Hf	178.6	Tantalum . . . Ta	180.95
Helium . . . He	4.003	Tellurium . . . Te	127.61
Holmium . . . Ho	164.94	Terbium . . . Tb	158.93
Hydrogen . . . H	1.0080	Thallium . . . Tl	204.39
Indium . . . In	114.76	Thorium . . . Th	232.05
Iodine . . . I	126.92	Thulium . . . Tm	168.94
Iridium . . . Ir	192.2	Tin . . . Sn	118.70
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¹ With corrections recommended in 1954 (*Chem. and Ind.*, 1954, 1136).

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